

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

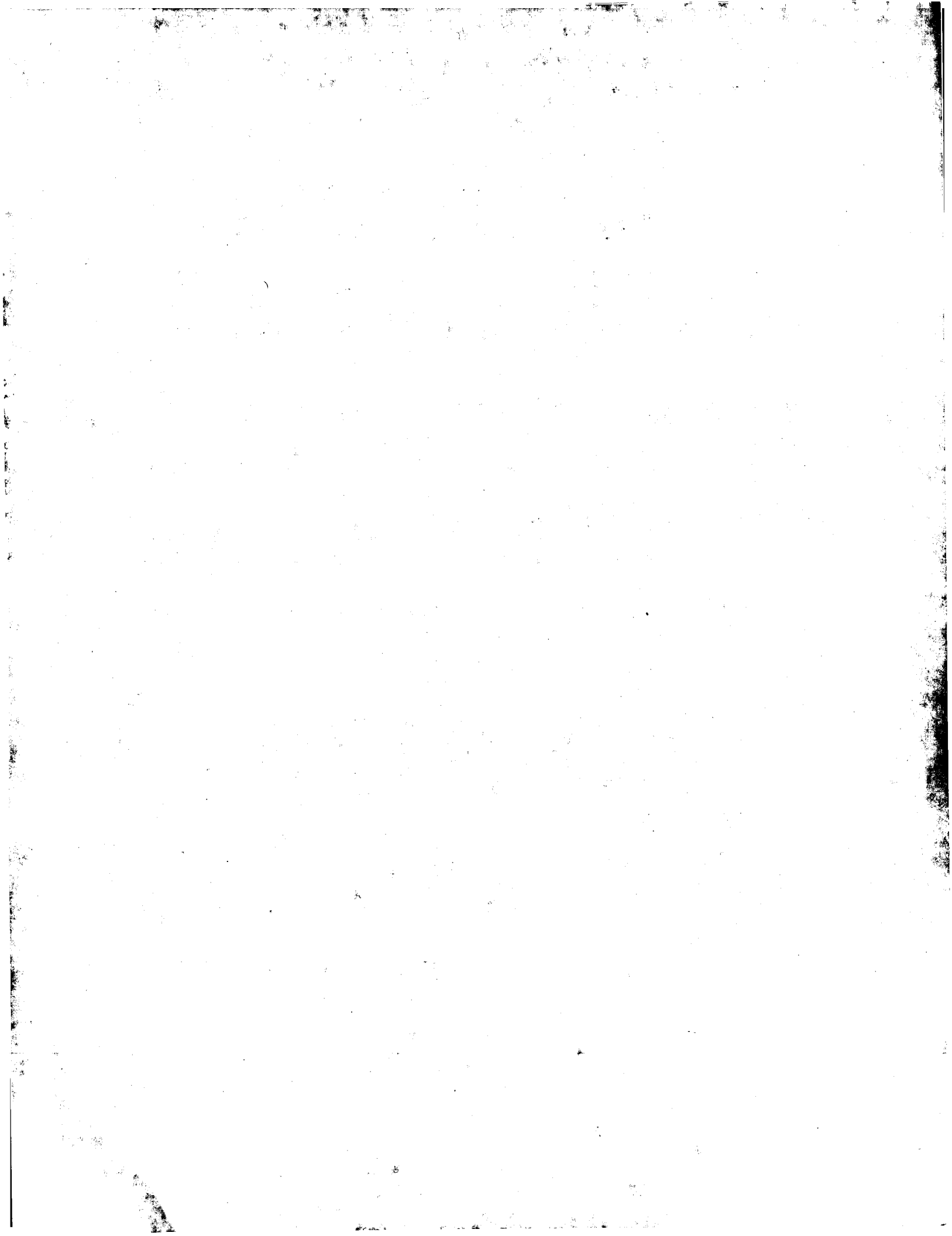
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 October 2001 (18.10.2001)

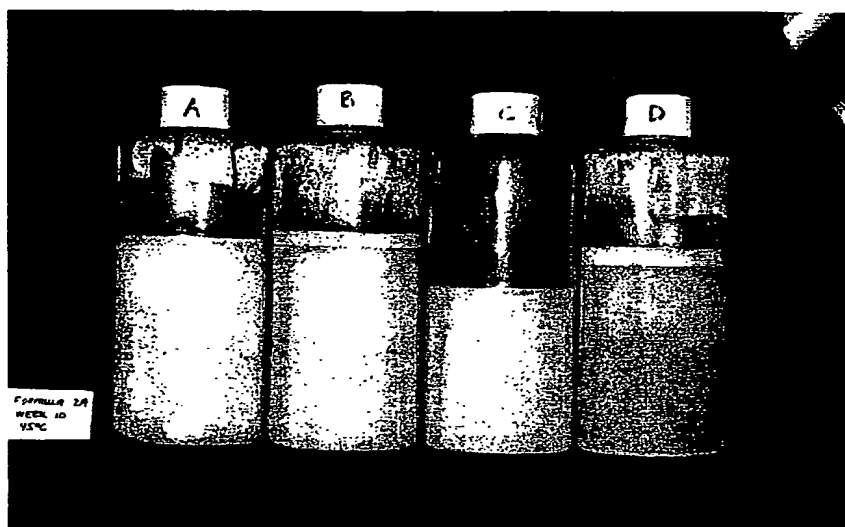
PCT

(10) International Publication Number
WO 01/76552 A2

- (51) International Patent Classification⁷: **A61K 7/50**, 7/48, 7/06
- (21) International Application Number: **PCT/US01/40480**
- (22) International Filing Date: **11 April 2001 (11.04.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
09/547,595 **11 April 2000 (11.04.2000)** **US**
- (71) Applicant: **NOVEON IP HOLDINGS CORP. [US/US];**
9911 Brecksville Road, Cleveland OH 44141-3247 (US).
- (72) Inventors: **SCHMUCKER-CASTNER, Julie, F.**; 15207 Parkwood Lane, Strongsville, OH 44136 (US). **AM-BUTER, Hal**; 3887 Ridge Road, Medina, OH 44256 (US). **SNYDER, Marcia**; 4580 Greenlawn, Stow, OH 44224 (US). **WEAVER, Ashley, A.**; 1301 S. Scott Street #329, Arlington, VA 22204 (US). **KOTIAN, Sahira, V.**; 40249 Dow Estates, Gonzales, LA 70737 (US).
- (74) Agent: **DUNLAP, Thoburn, T.**; Noveon, Inc., Law Department, 9911 Brecksville Road, Cleveland, OH 44141-3247 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— *without international search report and to be republished upon receipt of that report*

[Continued on next page]

(54) Title: **STABLE AQUEOUS SURFACTANT COMPOSITIONS**



Sample **A** **B** **C** **D**

(57) Abstract: A stable, aqueous composition containing a substantially crosslinked alkali-swellaable acrylate copolymer rheology modifier, a surfactant, an alkaline material, and various compounds therein, as for example substantially insoluble materials requiring suspension or stabilization, such as a silicone, an oily material, or a pearlescent material. Additionally, this invention also relates to the formation of a rheologically and phase stable cationic hair dye composition. The invention further relates to the incorporation of an acidic material after the addition of an alkaline material to reduce the pH of the composition without negatively impacting the viscosity of the composition.

WO 01/76552 A2



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

5 **STABLE AQUEOUS SURFACTANT COMPOSITIONS**

FIELD OF INVENTION

10 The present invention relates to the formation of stable, aqueous compositions containing a substantially crosslinked alkali-swelling acrylate copolymer rheology modifier, a surfactant, an alkaline material, and various compounds therein, as for example substantially insoluble materials requiring suspension or stabilization, such as a silicone, an oily material, or
15 a pearlescent material. Additionally, this invention also relates to the formation of a rheologically and phase stable cationic hair dye composition. The invention further relates to the incorporation of an acidic material after the addition of an alkaline material to reduce the pH of the composition without negatively impacting
20 the viscosity and rheology of the composition.

BACKGROUND OF THE INVENTION

25 Heretofore, various substantially insoluble compounds could not be adequately stabilized in an aqueous surfactant containing composition. For example, various aqueous surfactant compositions which contain silicone additives therein, as for example hair or skin conditioners, would separate and/or cream from their surfactant base. Various pearlescent materials, which
30 are often utilized to provide a pearlescent appearance, would have a short shelf life and produce a diminished pearlescent appearance ("flatten out") or actually settle. In other words,

-2-

instability problems generally existed with regards to the incorporation of silicones and pearlescent materials.

While cationic or basic dyes for hair have been utilized in shampoos to impart temporary color or highlights, the cationic dyes were generally incompatible with the anionic surfactants typically used in traditional shampoo formulas. Accordingly, amphoteric surfactants have been utilized to impart cleansing and detergency properties to the shampoos, but such surfactants do not sufficiently thicken to provide the desired product rheology. While traditional polymeric rheology modifiers, such as carbomers and/or acrylates/C₁₀₋₃₀ alkyl acrylate cross polymers, have been utilized to increase viscosity, the rheological stability of these compositions is still generally poor.

Various attempts have been made to remedy the above problems.

For example, U.S. Patent 5,656,257 relates to an anionic shampoo and conditioning composition comprising an oily conditioning agent, a shampooing agent, an acrylate copolymer, a cationic conditioning agent, and water. It also relates to the incorporation of a C₈-C₁₈ fatty acid. The composition utilizes both oily and cationic conditioning agents in combination with an anionic acrylate copolymer for maintaining stability and dispersion.

WO 99/21530 relates to a hair care composition comprising from about 1.00% to about 80.00% by weight of one or more surfactants selected from the group consisting of anionic, nonionic, cationic and zwitterionic surfactants and mixtures thereof; from about 0.05% to about 15.00% by weight of at least one fatty alcohol having from 10 to about 30 carbon

atoms; from about 0.10% to about 15.00% by weight of a non-volatile silicone; and from about 1.35% to about 2.70% by weight of a non-crosslinked polymeric suspending agent.

5 EPO 463,780 relates to a stable, pearly shampoo composition comprising insoluble, non-volatile silicone which may be obtained by including a suspending polymer, to prevent the silicone "creaming" to the top of the bottle in storage, and also to prevent the particles of titanium dioxide coated mica from settling. The composition further relates to an aqueous shampoo
10 composition comprising in addition to water:

- (a) from 2 to 40% by weight of a surfactant chosen from anionic, nonionic or amphoteric surfactants, or mixtures thereof;
- (b) from 0.01 to 10% by weight of an insoluble, non-
15 volatile silicone;
- (c) from 0.1 to 5% by weight of a suspending polymer chosen from polyacrylic acid, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-
20 containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, and heteropolysaccharide gums; and
- (d) from 0.01 to 5% by weight of titanium dioxide coated mica.

25 U.S. Patent No. 4,529,773 relates to compositions containing an associative thickener (a hydrophobically modified alkali-soluble emulsion polymer) that has been activated by neutralization to a pH above 6.5, and subsequently acidified in the presence of a surfactant.

However, the above prior art does not produce sufficiently stabilized aqueous surfactant compositions such as with respect to various silicones, oily materials, pearlescent materials, cationic hair dyes, and other substantially insoluble materials.

5

SUMMARY OF THE INVENTION

A stable aqueous composition comprises a substantially crosslinked alkali-swelling acrylate copolymer rheology modifier, water, an alkaline material, and an effective amount of a surfactant so that a substantially insoluble compound is stabilized or suspended in the composition. Compositions can be stabilized that contain various volatile and nonvolatile silicone oils, oily materials, and the like. Compositions containing a pearlescent material can be stabilized and which further impart an enhanced pearlescent appearance to the composition. Additionally, compositions containing cationic dyes can be attained and maintained with acceptable rheology. Furthermore, a "Back-Acid" formulation technique can be utilized to achieve low pH compositions. These stable aqueous surfactant compositions can generally maintain a smooth, acceptable rheology, without significant increases or decreases in viscosity or pH, with no separation, settling, or creaming out, over extended periods of time such as for at least one month at 45°C. The polymeric rheology modifier is generally made from one or more carboxylic acid monomers, vinyl monomers, and polyunsaturated monomers. The surfactant can be an anionic, an amphoteric, a zwitterionic, a nonionic, or a cationic surfactant, or combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photograph of containers of Example 2A
5 (pearlized 2-in-1 conditioning shampoo) showing stability testing
at 45°C for 10 weeks;

FIG. 2 is a photograph of containers of Example 2C
(pearlized 2-in-1 conditioning shampoo with mica) showing
stability testing at 45°C for 8 weeks;

10 FIG. 3 is a photograph of containers of Example 2C
(pearlized 2-in-1 conditioning shampoo with mica) showing the
initial appearance;

FIG. 4 is a photograph of containers of Example 2C
(pearlized 2-in-1 conditioning shampoo in mica) showing the
15 initial appearance (top) and after 12 hours (bottom);

FIG. 5 is a photograph of containers of Example 4A
(salicylic acid facial scrub) showing stability testing at 45°C for 8
weeks;

FIG. 6 is a photograph of containers of Example 4B
20 (salicylic acid shampoo with mica) showing stability testing at
45°C for 8 weeks;

FIG. 7 is a photograph of containers of Example 5
(pearlized mild body wash) showing stability testing at 45°C for
10 weeks;

25 FIG. 8 is a photograph of containers of Example 6 (clear
bath gel with suspended beads) showing stability testing at room
temperature for 8 weeks.

DETAILED DESCRIPTION OF THE INVENTION

The headings provided herein serve to illustrate, but not to limit the invention in any manner.

5

Polymeric Rheology Modifier

The polymeric rheology modifier provides various rheological properties, such as flow properties, thickening or viscosity, vertical cling, suspending ability, and Yield Value. Yield Value, also referred to as Yield Stress, is herein defined as the initial resistance to flow under stress. It can be measured using a number of techniques, such as via the use of a constant stress rheometer or via extrapolation using a Brookfield viscometer. These techniques and the usefulness of the Yield Value measurement are further explained in Technical Data Sheet Number 244 available from The B.F. Goodrich Company, herein incorporated by reference. In addition, the polymer is also useful to provide stabilization of insoluble materials, such as particulate matter or oily materials, in the formulation, as well as providing stability to the entire formulation.

20

The substantially crosslinked alkali-swellaable acrylate copolymer rheology modifier of the present invention can generally be prepared by various polymerization routes, such as emulsion, solution, precipitation, and the like, with emulsion polymerization generally being preferred. Emulsion polymerization is generally carried out at a pH of from about 2.5 to about 5.0, with at least three essentially ethylenically unsaturated components. Furthermore, none of these monomers are an associative monomer which is a copolymerizable surfactant

25

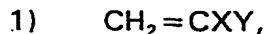
-7-

capable of nonspecific hydrophobic association similar to those of conventional surfactants.

The polymeric rheology modifier of the present invention generally comprises three structural components. The first
5 component is one or more carboxylic acid monomers having a total of from about 3 to about 10 carbon atoms. Examples of such monomers include but are not limited to acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, maleic acid, or aconitic acid. Moreover, half esters of polyacids, such as
10 maleic acid, fumaric acid, itaconic acid, or aconitic acid and the like with C₁₋₄ alkanols can also be used, particularly if it is used in minor amounts in combination with acrylic acid or methacrylic acid.

The amounts of such carboxylic acid monomers is
15 generally from about 20% to 80% by weight, desirably from about 25% to about 70% by weight and preferably from about 35% to about 65% by weight based upon the total weight of the monomers.

The second component is one or more non-acid vinyl
20 monomers which are utilized in an amount of from about 80% to about 15% by weight, desirably from about 75% to about 25% by weight, and preferably from about 65% to about 35% by weight based upon the total weight of the monomers. Such vinyl monomers are α,β -ethylenically unsaturated monomers
25 having the formula:



where X is H and Y is $-\text{COOR}$, $-\text{C}_6\text{H}_4\text{R}'$, $-\text{CN}$, $-\text{CONH}_2$, $-\text{Cl}$,
 $-\text{NC}_4\text{H}_6\text{O}$, $-\text{NH}(\text{CH}_2)_3\text{COOH}$, $-\text{NHCOCH}_3$, $-\text{CONHC}(\text{CH}_3)_3$,
 $-\text{CO-N}(\text{CH}_3)_2$,

-8-

or X is CH₃ and Y is -COOR, -C₆H₄R', -CN or -CH=CH₂;

or X is Cl and Y is Cl, and

R is C₁-C₁₈ alkyl, or hydroxy C₂-C₁₈ alkyl,

R' is H or C₁-C₁₈ alkyl

5 or having the formula:

2) CH₂=CH (OCOR¹);

where R¹ is C₁-C₁₈ alkyl;

or having the formula:

3) CH₂=CH₂ or CH₂=CHCH₃.

10

Typical of such vinyl monomers or mixture of monomers are the various acrylate or hydroxy acrylate esters wherein the ester portion has from 1 to 10 carbon atoms such as methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, 15 2-hydroxyethyl acrylate, or various vinyl acetates, or styrene, or vinyl chloride, or vinylidene chloride, or acrylonitrile, acrylamide, N,N,-dimethylacrylamide, t-butyl-acrylamide, and their methacrylate analogs.

15

20

The third component forming the acrylate rheology modifier is one or more polyunsaturated compounds. Monomeric unsaturated compounds carrying a reactive group that is capable of causing a formed copolymer to be crosslinked before, during, or after polymerization has taken place can also be used.

25

The various polyunsaturated compounds are utilized to generate either a partially or substantially-crosslinked three-dimensional network. Examples of such polyunsaturated compounds are the polyalkenyl ethers of sucrose, or polyalcohols; diallylphthalates, divinyl benzene, allyl (meth)acrylate, ethylene glycol di(meth)acrylate, methylene

bisacrylamide, trimethylolpropane tri(meth)acrylate, diallyl itaconate, diallyl fumarate, diallyl maleate, zinc (meth)acrylate, derivatives of castor oils or polyols made from ethylenically unsaturated carboxylic acid and the like, glycidyl methacrylate, 5 N-methylol acylamide or N-alkoxymethylacrylamide, alkoxy being C₁ to C₁₈ alcohol; hydroxy(meth)acrylate or (meth)acrylate end-capped caprolactones.

For those skilled in the art of making unsaturated derivatives, a reaction scheme such as an esterification reaction 10 of polyols made from ethylene oxide or propylene oxide or combinations thereof with unsaturated acid such as acrylic acid, methacrylic acid, or with unsaturated anhydride such as maleic anhydride, citraconic anhydride, itaconic anhydride, or an addition reaction with unsaturated isocyanate such as 15 3-isopropenyl- α - α -dimethylbenzene isocyanate, is also within the scope of the present invention. Wherever "(meth)" is utilized, it means that the use of the methyl group is optional.

The third component can be used in an amount from about 0.01 to about 5% by weight, desirably from about 0.03 to about 20 3% by weight, and preferably from about 0.05 to about 1% by weight based upon the total weight of all of the monomers forming said acrylate copolymer rheology modifier.

Furthermore, the crosslinked copolymer rheology modifier is generally free of any moieties derived from associative 25 monomers (i.e. copolymerizable surfactants). Generally free is defined as containing less than about 1% by weight, desirably less than about 0.5% by weight, and preferably less than about 0.2% by weight.

-10-

The partially or substantially crosslinked three dimensional network of the present invention can be made in any conventional manner such as set forth in U.S. Patent No. 4,138,380, or U.S. Patent No. 4,110,291 which are hereby fully
5 incorporated by reference. Generally, one or more monomers of the above noted carboxylic acid monomers, vinyl monomers, and polyunsaturated monomers are added to a reaction vessel which contains water therein. Suitable amounts of conventional or
10 typical emulsion polymerization surfactants such as sodium lauryl sulfate are added as well as emulsion type initiators, for example sodium or potassium persulfate, redox initiator, and the like. The reaction vessel can also contain a chain transfer agent. The temperature is then increased from about 60°C to about 100°C and polymerization commences. Optionally, during the reaction,
15 additional monomers are added over a period of time. Upon completion of the addition of the monomers, polymerization is allowed to run to completion generally by adding additional initiator.

Polymeric rheology modifiers of the present invention are
20 commercially available from The B.F. Goodrich Company under the name of Acrylates Crosspolymer. Preferred are the polymers which provide a viscosity in water of 500 to 10,000 cP (Brookfield RVT, 20 rpm) at 1% active polymer concentration at pH 6-8.

25 The amount of the one or more substantially crosslinked alkali-swellaable acrylate copolymers is generally from about 0.1% to about 10%, desirably from about 0.3% to about 5%, and preferably from about 0.5% to about 3% of active polymer based upon the total weight of the composition.

Surfactant

The stabilized compositions contain various surfactants such as anionic, amphoteric, zwitterionic, nonionic, cationic, or combinations thereof.

The anionic surfactant can be any of the anionic surfactants known or previously used in the art of aqueous surfactant compositions. Suitable anionic surfactants include but are not limited to alkyl sulfates, alkyl ether sulfates, alkaryl sulfonates, alkyl succinates, alkyl sulfosuccinates, N-alkoyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, alkylamino acids, alkyl peptides, alkoyl taurates, carboxylic acids, acyl and alkyl glutamates, alkyl isethionates, and alpha-olefin sulfonates, especially their sodium, potassium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulfates, alkyl ether phosphates and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide or propylene oxide units per molecule, and preferably contain 1 to 3 ethylene oxide units per molecule.

Examples of suitable anionic surfactants include sodium and ammonium lauryl ether sulfate (with 1, 2, and 3 moles of ethylene oxide), sodium, ammonium, and triethanolamine lauryl sulfate, disodium laureth sulfosuccinate, sodium cocoyl isethionate, sodium C12-14 olefin sulfonate, sodium laureth-6 carboxylate, sodium C12-15 pareth sulfate, sodium methyl cocoyl taurate, sodium dodecylbenzene sulfonate, sodium cocoyl

-12-

sarcosinate, triethanolamine monolauryl phosphate, and fatty acid soaps.

The nonionic surfactant can be any of the nonionic surfactants known or previously used in the art of aqueous surfactant compositions. Suitable nonionic surfactants include but are not limited to aliphatic (C_6 - C_{18}) primary or secondary linear or branched chain acids, alcohols or phenols, alkyl ethoxylates, alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), block alkylene oxide condensate of alkyl phenols, alkylene oxide condensates of alkanols, ethylene oxide/propylene oxide block copolymers, semi-polar nonionics (e.g., amine oxides and phosphine oxides), as well as alkyl amine oxides. Other suitable nonionics include mono or di alkyl alkanolamides and alkyl polysaccharides, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene sorbitol esters, polyoxyethylene acids, and polyoxyethylene alcohols. Examples of suitable nonionic surfactants include coco mono or diethanolamide, coco diglucoside, alkyl polyglucoside, cocamidopropyl and lauramine oxide, polysorbate 20, ethoxylated linear alcohols, cetearyl alcohol, lanolin alcohol, stearic acid, glyceryl stearate, PEG-100 stearate, and oleth 20.

Amphoteric and zwitterionic surfactants are those compounds which have the capacity of behaving either as an acid or a base. These surfactants can be any of the surfactants known or previously used in the art of aqueous surfactant compositions. Suitable materials include but are not limited to alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines, alkyl glycinate, alkyl carboxyglycinates, alkyl amphopropionates,

-13-

alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates wherein the alkyl and acyl groups have from 8 to 18 carbon atoms. Examples include cocamidopropyl betaine, sodium cocoamphoacetate, cocamidopropyl hydroxysultaine, and sodium cocamphopropionate.

The cationic surfactants can be any of the cationic surfactants known or previously used in the art of aqueous surfactant compositions. Suitable cationic surfactants include but are not limited to alkyl amines, alkyl imidazolines, ethoxylated amines, quaternary compounds, and quaternized esters. In addition, alkyl amine oxides can behave as a cationic surfactant at a low pH. Examples include lauramine oxide, dicetyldimonium chloride, cetrimonium chloride.

Other surfactants which can be utilized in the present invention are set forth in more detail in WO 99/21530, U.S. Patent No. 3,929,678, U.S. Patent No. 4,565,647, U.S. Patent No. 5,720,964, and U.S. Patent No. 5,858,948. Other suitable surfactants are described in McCutcheon's Emulsifiers and Detergents (North American and International Editions, by Schwartz, Perry and Berch) which is hereby fully incorporated by reference.

While amounts of surfactant can vary widely, amounts which are often utilized generally range from about 1% to about 80%, desirably from about 5% to about 65%, and preferably from about 6% to about 30% or most preferably from about 8% to 20% weight based upon the total weight of the composition.

Absence of Fatty Acids, Fatty Acid Esters and Fatty Alcohols

The stable, aqueous surfactant containing compositions of the present invention are generally free of "fatty" compounds such as fatty acids, fatty acid esters and fatty alcohols. Fatty acids can generally be classified as monocarboxylic acids which are derived from the hydrolysis of fats which generally have at least 8 or 10 carbon atoms and often at least 14 carbon atoms or more such as lauric acid, myristic acid, palmitic acid, stearic acid, and the like. Fatty acid esters are made from such fatty acids. The fatty alcohols, generally have at least 10 or 12 carbon atoms and more often from about 14 to about 24 carbon atoms that include lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, and the like. By the term "free of" is generally meant that the compositions of the present invention contain generally less than about 5%, 2% or about 1%, desirably less than about 0.5%, 0.2%, or about 0.1%, and preferably less than about 0.05%, 0.03%, or 0.01% by weight or less of fatty acid and/or fatty alcohol.

Insoluble Materials or Compounds

The materials or compounds which require stabilization can be soluble or insoluble in water. Such compounds include insoluble silicones, silicone gums, volatile and nonvolatile silicone oils, pearlescent materials, and other types of compounds set forth hereinbelow.

Silicones and Insoluble Oily Compounds

Silicone and oily compounds are often incorporated into a formulation for conditioning, especially on hair and skin, and to

-15-

improve or impart shine, gloss, water resistance, and or lubricity. These materials can also function as moisture barriers or protectants.

5 The silicone compound can be insoluble or soluble in water.

Suitable water-insoluble, non-volatile silicone materials include amodimethicone, amodimethicone macroemulsions or microemulsions, polyalkylsiloxanes, poly-arylsiloxanes, polyalkylarylsiloxanes, polysiloxane gums, and polyethersiloxane
10 copolymers. Preferred are high molecular weight polydimethylsiloxanes and emulsions thereof, dimethicones from low to high molecular weight, for example straight chain polydimethylsiloxanes (dimethicone) having a viscosity of from about 5 to about 100,000 centistokes (cS), and other silicone
15 materials such as dimethiconol, dimethiconol macroemulsion or microemulsion, phenyldimethicone, polymethylphenyl polysiloxanes, organopolysiloxanes, alkoxysiloxanes, polydiorganosiloxanes, polydimethylsiloxane copolymer, and polyaminofunctional silicone, i.e. polyalkylaryl siloxane
20 polyalkylsiloxane, and the like. Water-insoluble silicone materials may also be considered oily conditioning agents. Teachings directed to suitable water-soluble and insoluble silicone materials are found in U.S. Pat. Nos. 4,788,006; 4,341,799; 4,152,416; 3,964,500; 3,208,911; 4,364,837 and 4,465,619, all of which
25 are incorporated herein by reference.

Additional non-soluble, silicone materials which can be utilized include volatile silicones, for example cyclomethicone, or polydimethylsiloxane with a viscosity of 10 cS or less.

-16-

Suitable water-soluble silicones include polyether/polysiloxane block copolymers, such as dimethicone copolyol, and derivatives thereof.

5 Examples of commercially available silicone materials include Dow Corning 200, 345, 3225C, 929 Emulsion, 949 Emulsion, 1664 Emulsion, 1692 Emulsion, 1784 Emulsion, 2-1894 Microemulsion, 184 Emulsion; and General Electric SF-1202, SF18 (350), SF2169, Viscasil 60M, SM2658; and from B.F.Goodrich, such as B.F.Goodrich wax S, C, and F; and others.

10 Preferred silicone materials used as an oily conditioning agent are polydimethylsiloxanes which have the CTFA designation of dimethicone and which range in viscosity from 5 to 100,000 cS at 25°C, and dimethiconol, and emulsions thereof. A preferred dimethicone has a viscosity of about 60,000
15 cS and is available from Dow Corning or General Electric.

Other suitable oily materials or conditioning agents include, but are not limited to the following: mineral oils and saturated or unsaturated vegetable oils such as soybean oil, babassu oil, castor oil, cottonseed oil, Chinese tallow oil, crambe oil, perilia
20 oil, Danish rapeseed, rice bran oil, palm oil, palm kernel oil, olive oil, linseed oil, coconut oil, sunflower oil, safflower oil, peanut oil, corn oil, sesame oil, and avocado oil, as well as petrolatum; d-limonene, emollients, Vitamin E, and Vitamin A, and esters such as isopropylpalmitate, cetearyl octanoate, C12-15 alkylbenzoate,
25 octyl stearate, and other materials such as PPG-2 myristyl etherpropionate, and the like.

The silicone or the oily conditioning agent, or combinations thereof comprises between about 0.1% to about 20%, more preferably between about 0.3% to about 7% and most

-17-

preferably about 0.5% to about 5% by weight of the composition.

Pearlescent Material

5 Some formulations are often opacified by deliberately incorporating pearlescent materials therein to achieve a cosmetically attractive pearl-like appearance, known as pearlescence. Persons skilled in the art are aware of problems faced by formulators in consistently preparing a pearlescent
10 formulation. A detailed discussion is found in the article "Opacifiers and pearling agents in shampoos" by Hunting, *Cosmetic and Toiletries*, Vol. 96, pages 65-78 (July 1981), incorporated herein by reference.

 The pearlescent material includes titanium dioxide coated
15 mica, iron oxide coated mica, ethylene glycol mono-stearate, ethylene glycol distearate, polyethylene glycol distearate, bismuth oxychloride coated mica, myristyl myristate, guanine, glitter (polyester or metallic), and mixtures thereof. Other pearlescent materials can be found in U.S. Patent No. 4,654,207 and U.S.
20 Patent No. 5,019,376, herein incorporated by reference.

 Surprisingly, an improved or enhanced pearlescent appearance has been observed when incorporating said substantially crosslinked alkali-swelling acrylate polymers. A visually perceivable improved appearance is observed initially and
25 especially after the compositions have been aged for 24 hours, as compared to compositions not containing the polymer. Furthermore, the polymer further prevents the sedimentation or precipitation of the pearlescent material thus significantly decreasing the "flattening out" of the pearlescent appearance.

-18-

Additionally, it is believed that the polymeric rheology modifier serves to hold the pearlescent particles or platelets in their optimal configuration for maximum pearlescent appearance.

5 The amount of the pearlescent material can generally be used in amounts of from about 0.05% to about 10% and desirably from about 0.15% to about 3% by weight based upon the total weight of the stabilized composition.

Other Insoluble Compounds

10 In addition to the above generally insoluble compounds, numerous other optional substantially insoluble compounds which require stabilization can be utilized. Examples of such other insoluble compounds include Titanium Dioxide; Pumice; Calcium Carbonate; Talc; Potato Starch; Tapioca Starch; Jojoba
15 Beads; Polyethylene Beads; Walnut Shells; Loofah; Apricot Seeds; Almond Meal; Corn Meal; Paraffin; Oat Bran/Oat Hulls; Gelatin Beads; Alginate Beads; Stainless Steel Fibers; Iron Oxide Pigments; Air Bubbles; Mica Coated Iron Oxides; Kaolin Clay; Zinc Pyrithione; Salicylic Acid; Zinc Oxide; Zeolite; Styrofoam
20 Beads; Phosphates; silica, and the like. Other generally insoluble compounds include teatree powder, microsponges, confetti (a trademark of United Guardian Company), talc, beeswax, and the like.

25 The amount of the various insoluble compounds requiring stabilization will vary depending upon its purpose, desired end result, and efficacy thereof. Hence amounts can vary widely, but frequently will be within a general range of from about 0.1% to about 50% by weight based upon the total weight of the stable composition.

Cationic Dyes For Hair Coloring

The dyes which can be utilized in a temporary hair dye or color maintenance shampoo are generally soluble. Such dyes are generally known to the art and to the literature and are generally referred to as cationic or basic dyes. These dyes are commonly described in two different manners. The dye name (e.g. Basic Brown 16) relates to its INCI name (International Nomenclature Cosmetic Ingredient) and/or its CTFA name (Cosmetic, Toiletry and Fragrance Association) name. Another way to refer to these dyes is through its Color Index number (e.g. CI 12250) which is used by the European Union. Both sets of numbers are set forth in the "International Cosmetic Ingredient Dictionary and Handbook" for example, the 7th Edition, 1997, published by The Cosmetic, Toiletry, and Fragrance Association, Washington, D.C., U.S.A. These cationic dyes are commercially available from Warner Jenkinson under the trademark Arianor. Specific cationic dyes which can be utilized include the various azo dyes such as Basic Brown 16 (CI 12250), Basic Brown 17 (CI 12251), Basic Red 76 (CI 12245), Basic Yellow 57 (CI 12719), as well as various anthraquinone dyes such as Basic Blue 99 (CI 56059) and the like.

The amount of the hair dye when utilized in typical temporary color shampoos is generally from about 0.1 to about 5% by weight based upon the total weight of the stabilized composition.

Alkaline Material

The polymeric rheology modifiers of the present invention are generally supplied in their acidic form. These polymers modify the rheology of a formulation through subsequent neutralization of the carboxyl groups of the polymer. This causes ionic repulsion and a three dimensional expansion of the microgel network thus resulting in an increase in viscosity and other rheological properties. This is also referred to in the literature as a "space filling" mechanism as compared to an associative thickening mechanism.

The alkaline material is therefore incorporated to neutralize the polymer and is preferably a neutralizing agent. Many types of neutralizing agents can be used in the present invention, including inorganic and organic neutralizers. Examples of inorganic bases include but are not limited to the alkali hydroxides (especially sodium, potassium, and ammonium). Examples of organic bases include but are not limited to triethanolamine (TEA), L-arginine, aminomethyl propanol, tromethamine (2-amino 2-hydroxymethyl-1,3-propanediol), PEG-cocamine, diisopropanolamine, triisopropanolamine, or tetrahydroxypropyl ethylene diamine. Alternatively, other alkaline materials can be used, such as pre-neutralized surfactants or materials which incorporate a neutralizing agent therein or any other material capable of increasing the pH of the composition.

Acidic Materials

Various acidic materials can be utilized in the present invention such as organic acids, for example citric acid, acetic acid, alpha-hydroxy acid, beta-hydroxy acid, salicylic acid, lactic

acid, glycolic acid, or natural fruit acids, or inorganic acids, for example hydrochloric acid, nitric acid, sulfuric acid, sulfamic acid, phosphoric acid, and combinations thereof. Addition of the acidic materials can be at various points in the process, however, the addition of the acidic material after the addition of the alkaline neutralizing agents yields significantly improved rheological properties. This will be discussed in greater detail in the "back acid" formulation technique section.

10 Other Optional Rheology Modifiers

The composition can optionally contain other rheology modifiers to be used in conjunction with the substantially crosslinked alkali-swellaable acrylate copolymer. These polymers are well known in the art and can include natural, semi-synthetic (e.g. clays), or synthetic polymers. Examples of natural or modified natural polymers include but are not limited to gums (e.g., xanthan gum), cellulosics, modified cellulosics, starches, or polysaccharides. Examples of other synthetic polymers include but are not limited to cross-linked polyacrylates, hydrophobically modified alkali-soluble polymers, or hydrophobically modified nonionic urethane polymers. Additionally, the adjustment of viscosity by admixture of salt is also well known and can be employed in the present invention. If present in a composition, these rheology modifiers are generally used from about 0.01 to about 5% by weight of the stable composition.

Biologically Active Materials

The stable aqueous surfactant containing compositions of the present invention can also contain substantially insoluble

materials which are biologically active having pharmaceutical, veterinary, biocidal, herbicidal, pesticidal, or other biological activity. Specific examples of such biologically active compounds include acetazolamide; aescin; aesculi hippocastan; allantoine; amfepramone; aminopropylon; amorolfine; androstanolone; arnica; bamethan sulfate; benproperinembonate; benzalkonium chloride; benzocaine; benzoyl peroxide; benzyl nicotinate; betamethasone; betaxolol chlohydrate; buphenine hydrochloride; caffeine; calendula; campher; cetylpyridinium chloride; chloroquin phosphate; clarithromycin; clemastinhydrogene fumarate; clindamycin-2-dihydrogene phosphate; clobetasol-propionate; clotrimazole; codeine phosphate; croconazole; crotamiton; dexamethasone acetate; dexpanthenol; diclofenac; diethylamine salicylate; diflucortolone; diflucortolone valerate; diflucortolone, chlorquinaldol; difluoroprednate; dimethyl sulfoxide; dimeticone 350-silicium dioxide; dimetinden; dimetindenmaleat disopyramide; domperidone; ergotoxine; estradiol; estriol; etofenamate; felbinac; flubendazole; flufenamic acid; fluocinolone; fluocinolone acetonide; fluocortolone; fusidic acid; gelacturoglycani; heparine; hydrocortisone; hydroxyethyl salicylate; ibuprofen; idoxuridine; imidazole salicylate; indomethacin; isoprenaline sulfate; ketoprofen; levomenthol; lidocaine hydrochloride; lindane; menthol; mepyramine; mesalazine; methyl nicotinate; methyl salicylate; metronidazole; miconazole; minoxidil; naftifin; nalixidic acid; naproxen; niflumic acid; nifuratel; nifuratel nystatine; nifuroxazide; nitroglycerin; nonivamid; nystatinnifuratel; omoconazole nitrate; o-rutoside; oxatomide; oxerutin; oxyphenbutazone; pancreatine; pentosane

-23-

polysulfate; phenolphthalein; phenylbutazone-piperazine;
phenylephrine;
pilocarpine; piroxicam; plant extracts; polidocanol;
polycarbophil;
5 polysaccharide; potassium phosphate; prednisolone; prilocaine;
primycin sulphate lidocaine; progesterone; proteins;
racem.campher; retacnyl tritinoine; retinol palmitate;
salicylamide; salicylic acid; sobrerol; sodium alginate; sodium
bicarbonate; sodium fluoride; sodium pentosan polysulfate;
10 sodium phosphate; terpine; theophylline; thromboplastin;
thymol; tocopherol acetate; tolmetin; tretinoin; troxerutine;
verapamil; viloxazine; vitamine b6; xylitol; xylometazoline; and
zincum hyaluronicum; as well as combinations thereof.

Other compounds which can be utilized include the
15 following: 2-ethylhexyl salicylate; adapalene; albendazole;
avobenzene; benzalkonium chloride; benzocaine; benzoyl
peroxide; betamethasone dipropionate, betaxolo HCl; camphor;
capsaicin; clarithromycin; clindamycin phosphate; clobetasol
propionate; clocortolone pivalate; crotamiton; desoximetasone;
20 dimethicone; dioxybenzone; erythromycin; ethylhexyl p-
methoxycinnamate; fentoin; fluocinonide; guaifenesin;
homosalate; hydrocortisone; hydrocortisone valerate;
hydroquinone; kaolin; lidocaine; menthol; mesalamine; methyl
nicotinate; methyl salicylate; metronidazole; naftifine HCl;
25 nalidixic acid; nitrofurantoin monohydrate; octyl
methoxycinnamate; oxybenzone; padimate; pectin; permethrin;
phenylbenzimidazole sulfonic acid; phenylpropanolamine HCl;
pilocarpine HCl; piperonyl butoxide; prilocaine; progesterone;
pyrethrum extract; rimexolone; simethicone; sulfamethoxazole;

-24-

tretinoin; and zinc chloride; as well as combinations thereof.

Still other compounds which can be formulated into control release tablets and used in association with the present invention include: Ascorbic Acid; Aspirin; Atenolol;

- 5 Caramiphen HCl; Chlorpheniramine Maleate;
Dexchlorpheniramine; Diethyl Propion HCl; Diphenhydramine;
Ephedrine HCl; Furosemide; Guaifenesin; Isosorbide Dinitrate;
Isoanizid; Lithium Carbonate; Mepyramine Meleate; Methadone
HCl; Metoclopramide; Nitrofurantoin; Phenylpropanolamine HCl;
10 Pseudoephedrine; Quinidine Gluconate; Quinidine Sulfate;
Sodium Valproate; Sulfamethizole; Theophylline; Thiamine;
Tridecamine; Verapamil HCl; and Viloxazine; as well as
combinations thereof. These compounds are illustrative of
those which can be used. Other compounds known to those
15 skilled in the art may also be used.

Other ingredients

- In addition to the above noted compounds, various other ingredients can optionally be utilized in the stable composition of
20 the present invention such as Fragrances, Perfumes,
Preservatives, Disinfectants, Antioxidants, Antiredeposition
Agents, Carriers, Chelating and Sequestering Agents, Dyes and
Pigments, Quaternary Conditioners, Cationic conditioning
polymers such as guar hydroxypropyltrimonium chloride,
25 Polyquaternium-4, Polyquaternium-6, Polyquaternium-7,
Polyquaternium-10, Polyquaternium-11, Polyquaternium-16,
Polyquaternium-24, and Polyquaternium-39, Corrosion Inhibitors,
Hydrotropes, Coupling Agents, Defoamers, Builders, Dispersants,
Emollients, Extracts, Vitamins, Enzymes, Foam Boosters,

-25-

Flocculants, Whitening Agents, Fixative Polymers such as PVP, Humectants, Opacifiers, Plasticizers, Powders, Solubilizers, Solvents, Waxes, UV Absorbers/UV Light Stabilizers, Hydrolyzed Proteins, Keratin, Collagens, and the like.

5

Applications

The stable aqueous surfactant containing compositions of the present invention have a wide number of applications such as personal care applications, home care applications, industrial and institutional applications, pharmaceutical applications, textile compounds, and the like.

Examples of various personal care applications include products such as the following:

Shampoos, for example 2-in-1 Shampoos; Baby Shampoos; Conditioning Shampoos; Bodifying Shampoos; Moisturizing Shampoos; Temporary Hair Color Shampoos; 3-in-1 Shampoos; Anti-Dandruff Shampoos; Hair Color Maintenance Shampoos; Acid (Neutralizing) Shampoos; Salicylic Acid Shampoos;

Skin and Body Cleansers, for example Moisturizing Body Washes; Antibacterial Body Washes; Bath Gels; Shower Gels; Hand Soaps; Bar Soaps; Body Scrubs; Bubble Baths; Facial Scrubs; Foot Scrubs;

Creams and Lotions, for example Alpha-Hydroxy Acid Lotions and Creams; Beta-Hydroxy Acid Creams and Lotions; Skin Whiteners; Self Tanning Lotions; Sunscreen Lotions; Barrier Lotions; Moisturizers; Hair Styling Creams; Vitamin C Creams; Liquid Talc Products and Antibacterial Lotions; and other moisturizing lotions and creams;

-26-

Skin and Hair Gels, for example Facial Masks; Body Masks; Hydroalcoholic Gels; Hair Gels; Body Gels; Sunscreen Gels; and the like, as well as other personal care applications such as permanent hair color, and the like.

5 Examples of home care applications include products such as: home care and industrial and institutional applications, such as laundry detergents; dishwashing detergents (automatic and manual); hard surface cleaners; hand soaps, cleaners and sanitizers; polishes (shoe, furniture, metal, etc.); automotive
10 waxes, polishes, protectants, and cleaners, and the like.

 Examples of pharmaceutical applications include topical formulations in the form of creams, lotions, ointments, or gels, where the surfactant may be used as a wetting aid for the pharmaceutically active material, or as a skin penetration
15 enhancer, or as an emulsifier for a solvent phase having an aesthetic effect, or present to enhance the solubility or bioavailability of the pharmaceutically active material. Similar formulations for internal application within the living body, or oral administration, or administration by mechanical means, can be
20 utilized.

 These formulations could be administered or applied to either human or veterinary conditions for the full breadth of indications treatable by pharmaceutical means, such as fever, irritation, dermatitis, rash; viral, fungal, or bacterial infection;
25 organic disease; etc.

 The pharmaceutically active agents could have any appropriate function for treatment of the condition, and can be a mixture of one or more pharmaceutically active materials, such as emetics, antiemetics, febrifuge, fungicide, biocide, bactericide,

-27-

antibiotic, antipyretic, NSAID, emollient, analgesics, antineoplastics, cardiovascular agents, CNS stimulants, CNS depressants, enzymes, proteins, hormones, steroids, antipruritics, antirheumatic agents, biologicals, cough and cold
5 treatments, dandruff products, gastrointestinal treatment agents, muscle relaxants, psychotherapeutic agents, skin and mucous membrane agents, skin care products, vaginal preparations, wound care agents, and other appropriate classes of pharmaceutically active agents capable of appropriate
10 administration via dosage form.

Formulating Techniques

The present invention can be made in a number of ways. Generally the one or more substantially crosslinked alkali-swallowable acrylate copolymers are added to water and mixed.
15 The surfactant is subsequently added to the aqueous polymeric solution and mixed therein. (Alternatively, the surfactant can be added first to the water followed by the addition of the polymer.) An alkaline material, preferably a neutralizing agent, for example
20 sodium hydroxide, triethanolamine, etc, is then added and mixed to neutralize the solution. The remaining additives including the compound to be stabilized are then added with mixing to produce a desirable end product.

25 "Back-Acid" Formulating Technique

The polymeric rheology modifiers of the present invention do not start to build substantial viscosity until a pH of about 5 or 6 is achieved. There are some Home and Personal Care applications, however, that require a pH of less than 6 for

-28-

optimal and desired performance. This has limited the use of such polymers in such compositions. Additionally, it is difficult to even formulate stable applications at this lower pH range.

Surprisingly, it has now been found that if these
5 compositions are raised to a near neutral or even alkaline pH and then subsequently reduced in pH, the viscosity and yield value generally remain unchanged or often actually increase. This formulating technique will be herein referred to as "Back-Acid" thickening. This formulating technique thusly broadens the scope
10 of application of these polymers and now allows for formulation in the acidic pH regime. Additionally, the process of "Back-Acid" thickening can also be used to further increase the viscosity and stability of compositions formulated in the slightly acidic and in the alkaline pH regime.

15 The one or more acrylate copolymers, polymers, and the like are added to water and mixed. The surfactant is subsequently added to the aqueous polymeric solution and mixed therein. An alkaline material is then added and mixed to increase the pH of the composition to at least about 5, preferably at least
20 about 6, and most preferably at least about 6.5. The alkaline material is preferably a neutralizing agent, such as sodium hydroxide, potassium hydroxide, triethanolamine, or another fatty acid amine neutralizing agent commonly used in said applications. Alternatively, other alkaline materials can be used, such as pre-
25 neutralized surfactants. The pH should desirably be at least about 0.5 or 2 pH units and preferably at least 3, 4, or even 5 pH units above the final target pH of the composition. An acidic material is then added to reduce the pH of the composition.

-29-

The material used to decrease the pH of the application is an acidic material, preferably an organic acid, such as citric acid, acetic acid, alpha-hydroxy acid, beta-hydroxy acid, salicylic acid, lactic acid, glycolic acid, natural fruit acids, or combinations thereof. In addition, inorganic acids, for example hydrochloric acid, nitric acid, sulfuric acid, sulfamic acid, phosphoric acid, and combinations thereof can be utilized. The amount of such acid is generally from about 0.1 to about 20%, desirably from about 0.2% to 15%, and preferably from about 0.25% to about 10% by weight based upon the total weight of the stabilized composition.

The desired pH to stabilize compositions of the present invention is obviously dependent on the specific applications. Generally, Personal Care applications have a desired pH range of about 3 to about 7.5, desirably from about 4 to about 6. Generally, Home Care applications have a desired pH range of about 1 to about 12, and desirably from about 3 to about 10. More specifically, when a generally insoluble silicone or pearlescent compound is utilized, a desired pH is from about 5.5 to about 12, whereas when a hair dye is stabilized, the pH is from about 5 to about 9.

Stability:

The various personal care, home care, industrial, institutional, etc. products or compositions made using the substantially crosslinked alkali-swelling acrylate copolymer rheology modifier of the present invention are stable. The stability requirements for a particular composition will vary with its end marketplace application as well as the geography in which

-30-

it is to be bought and sold. An acceptable "shelf life" is subsequently determined for each composition. This refers to the amount of time that a composition should be stable across its normal storage and handling conditions, measured between the time that the composition is produced and when it is finally sold for consumption. Generally, Personal Care compositions require a 3 year shelf life whereas Home Care compositions require a 1 year shelf life.

To eliminate the need to conduct stability studies in excess of one year, the formulator will conduct stability testing at stressed conditions in order to predict the shelf life of a composition. Typically, accelerated testing is conducted at elevated static temperatures, usually 45-50°C. A composition should be stable for at least 2 weeks, desirably 1 month, preferably 2 or 3 months, and most preferably 4 or 5 months at 45°C. Additionally, freeze-thaw cycling is often employed wherein the composition is cycled between a freezing temperature, usually 0°C, and an ambient temperature, usually 20-25°C. A composition should pass a minimum of 1 freeze-thaw cycle, preferably 3 cycles, and most preferably 5 cycles.

Products or compositions made according to the present invention are considered stable if they meet one or more of the following criteria:

1. There is no phase separation, settling, or creaming of any material in the composition. The composition should remain completely homogenous throughout its bulk. Separation is herein defined as the visible existence of 2 or more distinct layers or phases of any component in the

-31-

formulation, including but not limited to insoluble matter, soluble matter, oily substances and the like.

2. The viscosity of the composition does not significantly increase or decrease over time, generally less than 50%, preferably less than 35%, and most preferably less than 20%.
3. The pH of the composition does not increase or decrease more than two pH units, preferably not more than one unit, and most preferably not more than one-half unit.
4. The rheology and texture of the composition does not significantly change over time to that which is unacceptable.

Products or compositions made according to the present invention are considered unstable if they do not meet one or more of the above listed criteria.

Further information on stability testing requirements can be found in "The Fundamentals of Stability Testing; IFSCC Monograph Number 2", published on behalf of the International Federation of Societies of Cosmetic Chemists by Micelle Press, Weymouth, Dorset, England, and Cranford, New Jersey, U.S.A. and is herein incorporated by reference.

Further information on stability of biologically active formulations can be found at: The European Union for the Evaluation of Medicinal Products/Documents Section/ ICH Guidelines: <http://www.eudra.org/humandocs/humans/ich.htm>. (Topic Q1A, Step 2) Note for Guidance on Stability Testing of New Drug Substances and Products (Revision of CPMP/ICH/380/95, released for consultation Nov. 99).

-32-

Examples

The invention will be better understood by reference to the following examples which serve to illustrate but not to limit the scope of the present invention.

In some of the following examples, the formulations were prepared as follows. The noted acrylate copolymer was added to water and mixed. Then, the surfactant was added to the aqueous polymer composition and mixed. Subsequently, the indicated neutralizing agent such as sodium hydroxide was added and mixed. The remaining compounds or ingredients were then added in the order listed with mixing upon the addition of generally each ingredient. Optionally, an acid such as citric acid was subsequently added and mixed.

-33-

FORMULATION EXAMPLES

EXAMPLE 1: Pearlized 3-In-1 Conditioning Shampoo

This formulation demonstrates:

- 1) A stable, aqueous surfactant composition using the "Back-Acid" formulation technique
- 2) Stabilization of an insoluble, high molecular weight non-volatile silicone emulsion
- 3) Suspension and stabilization of a pearlescent material
- 4) Enhanced pearlescent appearance

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A			
Deionized Water	qs	Diluent	
Acrylates Crosspolymer (30%)	4.00	Rheology Modifier	(BFGoodrich)
Sodium Laureth Sulfate (2 mole, 25%)	25.0	Primary Surfactant	Standapol ES-2 (Henkel)
Sodium hydroxide (18%)	0.75	Neutralizer	
PART B			
Deionized Water	5.00	Diluent	
NaOH (18%)	0.05	pH Adjuster	
Guar Hydroxypropyl Trimonium Chloride	0.30	Conditioner	Cosmedia Guar C-261N (Henkel)
PART C			
Lauryl Glucoside (50%)	4.00	Co-Surfactant	Plantaren 1200N (Henkel)
Sodium Lauryl Sulfate (29%)	15.0	Co-Surfactant	Standapol WAQ-Special (Henkel)
Glycol Distearate (and) Laureth-4 (and) Cocamidopropylbetaine	3.00	Pearlizing Agent	Euperlan PK-3000 (Henkel)
Dimethicone (and) Laureth-4 (and) Laureth-23	3.00	Conditioning Agent	DC 1664 Emulsion (Dow Corning)
Cocamidopropylbetaine (35%)	3.00	Foam Booster	Velvetex BA-35 (Henkel)
Coco-Glucoside (and) Glyceryl Oleate	1.00	Moisturizer	Lamesoft PO-65 (Henkel)
Fragrance	0.50	Aesthetic Enhancer	
Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.50	Preservative	Phenonip (Nipa)
Citric Acid (50%)	0.40	pH Adjuster	

Properties:

Appearance	Satiny, pearlized viscous liquid
pH	5.5 - 5.8
Viscosity* (cP)	8,000 - 10,000
Yield Value** (dynes/cm ²)	140 - 160
Surfactant Actives (%)	13.7
Stability	Passed 3 months accelerated, 45°C, Passed 5 cycles freeze/thaw

- * Brookfield DV-II+ (or RVT) @ 20, # 5 spindle
- ** Brookfield DV-II+ (or RVT) @1 and 0.5 rp

-34-

EXAMPLES 2A, 2B AND 2C: Pearlized 2-In-1 Conditioning Shampoo

These formulations demonstrate:

- 5 1) Stable, aqueous surfactant compositions using the "Back-Acid" formulation technique
- 2) Stabilization of an insoluble, high molecular weight non-volatile silicone
- 3) Suspension and stabilization of three different types of pearlescent materials: Guanine, Ethylene glycol distearate, and mica
- 4) Enhanced pearlescent appearance

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A			
Deionized Water	qs	Diluent	
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Sodium Laureth Sulfate, (3 mole, 28%)	30.00	Primary Surfactant	Standapol ES-3 (Henkel)
Sodium hydroxide (18%)	1.00	Neutralizer	
Cocoamidopropyl Hydroxysultaine (50%)	10.00	Co-Surfactant	Mirataine CBS (Rhodia)
Disodium Laureth Sulfosuccinate (40%)	10.00	Co-Surfactant	Mackanate EL (McIntyre)
PART B			
Deionized Water	qs	Diluent	
Pearlizing Agents:			
<u>Example 2A:</u>			
Guanine	0.15	Aesthetic Enhancer	Mearlmaid AA
<u>Example 2B:</u>			
Glycol distearate surfactant blend	3.00	Aesthetic Enhancer	Euperlan PK3000
<u>Example 2C:</u>			
Mica (and) Titanium Dioxide	0.20	Aesthetic Enhancer	Timiron MP115
PART C			
Dimethicone	3.00	Conditioner	Dow Corning 200 Fluid (60,000cS)
Fragrance	0.50	Aesthetic Enhancer	
Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.50	Preservative	Phenonip (Nipa)
Citric Acid (50%)	0.35	pH Adjuster	

Properties:

10	Appearance	Viscous, satiny, pearlized liquid
	pH	5.4 - 5.7
	Viscosity* (cP)	2A = 3,600 - 6,000 2B = 5,300 - 8,200 2C = 3,600 - 6,000
15	Yield Value** (dynes/cm ²)	80 - 150
	Surfactant Actives (%)	17.4
	Stability	Passed 3 months accelerated, 45°C Passed 5 cycles freeze/thaw

20

- * Brookfield DV-II+ (or RVT) @ 20 rpm, 25°C, #4 RV spindle
- ** Brookfield DV-II+ (or RVT) @1 and 0.5 rpm

-35-

EXAMPLE 3A AND 3B: Clear or Brilliant Gold Pearlized 2-In-1 Conditioning Shampoo

These two formulations are examples of 2-in-1 conditioning shampoos formulating using the "Back-Acid" technique. They also demonstrate the stabilization of an insoluble, non-volatile, high molecular weight amine-functional silicone microemulsion.

Example 3A is a clear formulation at a low pH (about 5).

Example 3B further contains a pearlescent material which is suspended and stabilized. This example also demonstrates the ability of the rheology-modifying polymer to enhance the pearlescent appearance of the formulation.

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A			
Deionized Water	qs	Diluent	
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Ammonium Lauryl Sulfate (30%)	40.00	Primary Surfactant	Stepanol AM (Stepan)
Ammonium Laureth Sulfate (3 mole, 27%)	20.00	Primary Surfactant	Standapol EA-3 (Henkel)
NaOH (18%)	1.40	Neutralizer	
Ammonium Xylene Sulfonate (40%)	2.50	Hydrotrope	Stepanate AXS (Stepan)
PPG-2 Hydroxyethyl Cocoamide (100%)	4.00	Foam Booster	Promidium CO (Mona)
Disodium Cocoamphoacetate (50%)	4.00	Mild Surfactant	Monateric CLV (Mona)
PART B			
Deionized Water	qs	Diluent	
EXAMPLE 3A:			
Does not contain Mica			
EXAMPLE 3B:			
Mica, Titanium Dioxide and Iron Oxides	0.20	Aesthetic Enhancer	Cloisonné Sparkle Gold #222J (Englehard)
PART C			
Amodimethicone (and) Trideceth-12 (and) Cetrimonium Chloride	3.00	Conditioner	Dow Corning 2-8194 Microemulsion
Fragrance	0.50	Aesthetic Enhancer	
Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.50	Preservative	Phenonip (Nipa)
Citric Acid (50%)	1.70	pH Adjuster	

Properties:

Appearance

3A = Clear, viscous liquid

3B = Viscous, gold, pearlized liquid

-36-

	<u>Addition</u>	<u>Before Citric Acid Addition</u>	<u>After Citric Acid</u>
	pH	6.5	5.0
	Viscosity* (cP)	3,300	7,800
5	Yield Value** (dynes/cm ²)	22	180
	Surfactant Actives (%)	24.4	
	Stability	Passed 3 months accelerated, 45°C	
		Passed 5 cycles freeze/thaw	
10			
	* Brookfield DV-II+ (or RVT) @ 20 rpm, 25°C, #5 RV spindle		
	** Brookfield DV-II+ (or RVT) @1 and 0.5 rpm		

* Brookfield DV-II+ (or RVT) @ 20 rpm, 25°C, #5 RV spindle

** Brookfield DV-II+ (or RVT) @1 and 0.5 rpm

-37-

EXAMPLE 4A AND 4B: Salicylic Acid Facial Scrub or Shampoo

These two formulations are examples of a salicylic acid facial scrub at a very low pH formulated using the "Back-Acid" technique.

Example 4A demonstrates the suspension and stabilization of an insoluble material, jojoba beads, at a very low pH (about 4)

Example 4B contains a pearlescent material which is suspended and stabilized. This example also demonstrates the ability of the rheology-modifying polymer to enhance the pearlescent appearance of the formulation.

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A			
Deionized Water	qs	Diluent	
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Alpha Olefin Sulfonate (40%)	15.00	Primary Surfactant	Bioterge AS-40 (Stepan)
Sodium hydroxide (18%)	1.00	Neutralizer	
Citric Acid (50%)	0.50	pH Adjuster	
PART B			
Deionized Water	15.00	Diluent	
Alpha Olefin Sulfonate (40%)	10.00	Primary Surfactant	Bioterge AS-40 (Stepan)
Glycerin	2.00	Emollient	
Salicylic Acid (USP)	2.00	Active	
PART C			
Cocamidopropylbetaine (35%)	10.00	Foam Booster	Velvetex BA-35 (Henkel)
FOR EXAMPLE 4A :			
Potassium C ₁₂₋₁₃ Phosphate (40%)	2.00	Mild Surfactant	Monafax MAP 230 (Mona)
FD&C Red #33 (0.1%)	0.10	Aesthetic Enhancer	(BFG Hilton Davis)
FD&C Yellow #6 (0.1%)	0.20	Aesthetic Enhancer	(BFG Hilton Davis)
Jojoba Beads	2.00	Aesthetic Enhancer	Florabeads (Floritech)
FOR EXAMPLE 4B:			
Deionized water	qs	Diluent	
Mica (and) Titanium Dioxide	0.20	Aesthetic Enhancer	Timiron MP 115 (Rona)

Properties:

Appearance

4A = Translucent, viscous liquid with suspended beads

4B = Satiny, white, pearlized viscous

liquid

pH

3.8 - 4.0

Viscosity* (cP)

5,500 - 10,000

Yield Value** (dynes/cm²)

200 - 350

Surfactant Actives (%)

14.3

Stability

Passed 3 months accelerated, 45°C

Passed 5 cycles freeze/thaw

* Brookfield DV-II+ (or RVT) @ 20 rpm, 25°C, #4 RV spindle

** Brookfield DV-II+ (or RVT) @1 and 0.5 rpm

-38-

EXAMPLE 5: Pearlized Mild Body Wash

The following formulation is an example of a pearlized mild body wash. This formulation demonstrates the following:

- 1) A stable, aqueous surfactant composition using the "Back-Acid" formulation technique
- 2) Stabilization of an insoluble, high molecular weight non-volatile silicone gum emulsion
- 3) Suspension and stabilization of a pearlescent material
- 4) Enhanced pearlescent appearance

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A			
Deionized Water	14.45	Diluent	
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Cocoyl Isethionate (and) Sodium Lauroamphoacetate (and) Sodium Methyl Cocoyl Taurate (and) Sodium Xylene Sulfonate (38%)	45.00	Primary Surfactant Blend	Miracare UM-140 (Rhodia)
Sodium Laureth Sulfate (2 mole, 27%)	15.00	Primary Surfactant	Rhodapex ES-2 (Rhodia)
PART B			
Deionized Water	5.00	Diluent	
NaOH (18%)	0.05	pH Adjuster	
Guar Hydroxypropyl Trimonium Chloride	0.15	Conditioning Agent	Jaguar C-14S (Rhodia)
Citric Acid (50%)	0.05	pH Adjuster	
PART C			
Sodium Cocoamphoacetate (37%)	5.00	Co-Surfactant	Miranol Ultra C37 (Rhodia)
Polyquaternium-7	2.00	Conditioner	Mirapol 550 (Rhodia)
Dimethiconol (and) TEA-Dodecylbenzenesulfonate	4.00	Conditioner	DC 1784 Emulsion (Dow Corning)
PART D			
Deionized Water	2.50	Diluent	
Mica (and) Titanium Dioxide	0.20	Aesthetic Enhancer	Flamenco Satin Pearl 3500 (Englehard)
PART E			
Fragrance	0.50	Aesthetic Enhancer	
Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.50	Preservative	Phenonip (Nipa)
Citric Acid (50%)	0.60	pH Adjuster	

Properties:

Appearance	Viscous, satiny, pearlized liquid
pH	6.4 - 6.8
Viscosity* (cP)	17,000 - 22,000
Yield Value** (dynes/cm ²)	100 - 150
Surfactant Actives (%)	23.0
Stability	Passed 3 months accelerated, 45°C Passed 5 cycles freeze/thaw
* Brookfield DV-II+ (or RVT) @ 20 rpm, 25°C, #6 RV spindle	
** Brookfield DV-II+ (or RVT) @1 and 0.5 rpm	

-39-

EXAMPLE 6: Clear Bath Gel with Suspended Beads

The following formulation is an example of a clear bath gel with suspended beads. This formulation demonstrates the following:

- 1) A stable, aqueous surfactant composition
- 2) Suspension and stabilization of an insoluble material, gelatin beads with mineral oil

Ingredient	Weight Percent	Function	Trade Name (Supplier)
Deionized Water	qs	Diluent	
Acrylates Crosspolymer (30%)	8.00	Rheology Modifier	(BFGoodrich)
Sodium Laureth Sulfate (2 mole, 28%)	37.30	Primary Surfactant	Texapon NSO (Henkel)
Sodium hydroxide (18%)	1.32	Neutralizer	
Cocamidopropylbetaine (30%)	2.10	Foam Booster	Tegobetaine L (Goldschmidt)
Polyquaternium -39	2.10	Conditioning Agent	Merquat 3330 (Calgon)
Tetrasodium EDTA	0.05	Chelating Agent	
Fragrance	0.50	Fragrance	
Polysorbate 20	0.50	Solubilizer	Tween-20
White Beads with Vitamin E	1.00	Moisturizer	Lipopearls (Lipo Technologies)

Properties:

Appearance	Viscous, clear liquid
pH	6.3-6.7
Viscosity* (cP)	4,000 – 6,000 cP
Yield Value** (dynes/cm ²)	120-220
Surfactant Actives (%)	11.1
Stability	Passed 3 months accelerated 45°C
	Passed 5 cycles freeze/thaw

* Brookfield DV-II + (or RVT) @ 20 rpm, 25°C, #4 RV spindle

** Brookfield DV-II + (or RVT) @1 and 0.5 rpm

EXAMPLE 7: Temporary Color Shampoo (Medium Brown)

The following formulation is an example of a temporary color shampoo or color maintenance shampoo. This formulation demonstrates the following:

- 5
- 1) A stable viscous temporary hair color composition using cationic dyes
 - 2) Suspension and stabilization of a pearlescent material
 - 3) Enhanced pearlescent appearance
 - 4) Improved rheological properties

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A			
Deionized water	41.85	Diluent	
Acrylates Crosspolymer (30%)	10.00	Rheology modifier	(BFGoodrich)
PART B			
Deionized water (heated to 50°C)	15.00	Diluent	
Disodium EDTA	0.05	Chelator	
Butylene Glycol	5.00	Solvent	
Sodium cocoamphoacetate (37%)	15.00	Surfactant	Miranol Ultra C-37 (Rhodia)
Cocamidopropyl betaine (35%)	3.00	Surfactant	Proteric CAB (Protameen)
Polyquaternium-39	0.80	Hair conditioner	Merquat Plus 3330 (Calgon)
Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben	0.45	Preservative	Germaben II (ISP)
Sodium Hydroxide (18%)	0.25	Neutralizer	
PART C			
Deionized water (heated to 50°C)	10.00	Diluent	
Basic Brown 17/CI 12251	0.25	Dye	Arianor Sienna Brown (Tri-K/Warner Jenkinson)
Basic Blue 99/CI 56059	0.125	Dye	Arianor Steel Blue (Tri-K/Warner Jenkinson)
Basic Red 76/CI 12245	0.125	Dye	Arianor Madder Red (Tri-K/Warner Jenkinson)
Dimethicone copolyol	0.20	Hair conditioner	DC 193 Surfactant (Dow Corning)
PART D			
Decyl glucoside (50%)	4.00	Surfactant	Plantaren 2000 (Henkel Cospha)
Deionized water	3.00	Diluent	
Mica (and) Titanium dioxide	0.20	Pearlizing agent	Timiron MP-149 Diamond Cluster (Rona)

-41-

Properties:

	Appearance	Dark brown, pearlescent viscous liquid
	pH	6.8 – 7.4
5	Viscosity* (cP)	5,000 – 7,000
	Yield Value** (dynes/cm ²)	300 – 400
	Surfactant Actives (%)	8.6
	Stability	Passed 3 months accelerated, 45°C
10		Passed 7 cycles freeze/thaw

* Brookfield DV-II+ (or RVT) @ 20 rpm, #4 spindle

** Brookfield DV-II+ (or RVT) @1 and 0.5 rpm

EXAMPLE 8: Anti-Dandruff Shampoo

The following formulation is an example of a conditioning anti-dandruff shampoo. This formulation demonstrates the following:

- 5 1) A stable, aqueous surfactant composition using the "Back-Acid" formulation technique
- 2) Stabilization of an insoluble, high molecular weight non-volatile silicone gum emulsion
- 10 3) Suspension and stabilization of an insoluble anti-dandruff material; zinc pyrithione

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A			
Deionized Water	qs	Diluent	
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Sodium Lauryl Sulfate (29%)	16.00	Primary Surfactant	Standapol WAQ-LC (Henkel)
Sodium Laureth Sulfate (2 mole, 25%)	16.00	Primary Surfactant	Standapol ES-2 (Henkel)
Sodium hydroxide (18%)	0.65	Neutralizer	
PART B			
Deionized Water	10.00	Diluent	
Polyquaternium-10	0.25	Hair Conditioner	Ucare Polymer JR-400 (Amerchol)
DMDM Hydantoin	0.30	Preservative	Glydant (Lonza)
PART C			
Cocamidopropylbetaine (35%)	4.00	Foam Enhancer	Velvetex BA-35 (Henkel)
Citric Acid (50%)	0.75	pH Adjuster	
Zinc Pyrithione (48%)	2.50	Active	Zinc Omadine (Arch Chemical)
Dimethiconol (and) TEA-	3.00	Conditioner	DC 1784 Emulsion (Dow Corning)
Dodecylbenzenesulfonate			
FD&C Blue #1 (0.1%)	1.00	Dye	(BFG Hilton Davis)
Fragrance	0.50	Fragrance	
Sodium Chloride	0.60	Viscosity Enhancer	

Properties:

15	Appearance	Blue, opaque, viscous liquid
	pH	5.4 - 5.7
	Viscosity* (cP)	3,500 - 5,000
	Yield Value** (dynes/cm ²)	120-170
	Surfactant Actives	11.5
20	Stability	Passed 1 month accelerated, 45 °C

- * Brookfield DV-II + (or RVT) @ 20 rpm, 25 °C, #4 spindle
- ** Brookfield DV-II + (or RVT) @ 1 and 0.5 rpm

-43-

EXAMPLE 9: Clear Bath Gel with Suspended Beads

The following formulation is an example of a clear bath gel with suspended beads. This formulation demonstrates the following:

- 5 1) A stable, aqueous surfactant composition
 2) Suspension and stabilization of an insoluble material, gelatin beads with mineral oil

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A			
Deionized Water	42.03	Diluent	
Acrylates Crosspolymer (30 %)	10.00	Rheology Modifier	(BFGoodrich)
Sodium Laureth Sulfate (3 mole, 28%)	30.00	Primary Surfactant	Standapol ES-3 (Henkel)
Sodium hydroxide (18%)	1.90	Neutralizer	
Propylene Glycol	2.00	Humectant	
PART B			
Deionized Water	5.00	Diluent	
Benzophenone-4	0.02	UV Absorber	Uvinul MS-40 (BASF)
Disodium EDTA	0.10	Chelating Agent	
PART C			
Cocoamidopropylbetaine (35%)	4.00	Foam Enhancer	Incronam 30 (Croda)
PART D			
Polysorbate 20	0.80	Solubilizer	Tween 20 (ICI)
Fragrance	0.60	Fragrance	
Propylene Glycol, Diazolidinyl Urea, Methylparaben, Propylparaben	1.00	Preservative	Germaben II (Sutton)
White Beads w/ Vitamin E	1.00	Moisturizer	Lipopearls (Lipo Technologies)
FD&C Blue #1 (0.1%)	0.05	Dye	(BFG Hilton Davis)
FD&C Green #5 (0.1%)	1.50	Dye	(BFG Hilton Davis)

Properties:

Appearance

Viscous, clear liquid

Before Citric Acid Addition

After Citric Acid

Addition

15 pH	6.5	4.5
Viscosity* (cP)	4,600	5,500
Yield Value** (dynes/cm ²)	270	440
Surfactant Actives (%)	10.6	
20 Stability	Passed 3 months accelerated, 45°C	
	Passed 5 cycles freeze/thaw	

* Brookfield DV-II + (or RVT) @ 20 rpm, 25°C, #4 RV spindle

** Brookfield DV-II + (or RVT) @1 and 0.5 rpm

25

-44-

EXAMPLE 10: Alpha Hydroxy Acid Cream

The following formulation is an example of an AHA (alpha-hydroxy acid) lotion. This formulation demonstrates the following:

- 5 1) A stable, aqueous surfactant-based emulsion composition using the "Back-Acid" formulation technique.
- 2) Rheology modification and stabilization of an emulsion containing a high level of an alpha hydroxy acid (about 6%) at a very low pH (about 4)
- 10 3) Stabilization of insoluble, non-volatile silicone (dimethicone) and other oily materials (isopropyl palmitate and mineral oil) in an emulsion

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A			
Deionized Water	51.55	Diluent	
Glycerin	4.80	Humectant	
Triethanolamine (99%)	0.75	Neutralizing Agent	
PART B			
Cetyl Alcohol	2.85	Opacifier	
Glyceryl Stearate (and) PEG-100 Stearate	4.25	Emulsifier	Arlacel 165 (ICI Surfactants)
Stearic Acid (3X)	1.45	Emulsifier	
Isopropyl Palmitate	4.25	Emollient	
Mineral Oil (and) Lanolin Alcohol	4.25	Emollient	Amerchol 101 (Amerchol)
Dimethicone	1.45	Emollient	DC 200 Fluid (350 cS) (Dow Corning)
PART C			
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Lactic Acid (45% Soln.)	13.40	Active	
Triethanolamine	5.00	Neutralizer	
Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben	1.00	Preservative	Germaben II (Sutton)

Properties:

15	Appearance	Thick, white cream
	pH	3.8 - 4.1
	Viscosity* (cP)	16,000 - 18,000
	Surfactant Actives (%)	5.7
	Stability	Passed 1 month accelerated, 45°C
20		Passed 3 cycles freeze/thaw
	* Brookfield DV-II+ (or RVT) @ 20 rpm, 25°C, #6 RV spindle	

Preparation Procedure:

1. Part A: Add glycerin and triethanolamine to deionized water. Heat to 65°C.
- 25 2. Part B: Combine all in separate vessel and heat until melted. Add to Part A with vigorous agitation. Allow to cool to ~40°C with mixing.
3. Slowly add in the Acrylates Crosspolymer while mixing.
4. Slowly add lactic acid solution while mixing.
5. Adjust pH to 4.0 with triethanolamine.
- 30 6. Add the preservative.

-45-

EXAMPLE 11: Facial Cream

The following formulation is an example of a facial cream. This formulation demonstrates the following:

- 1) An aqueous surfactant-based emulsion composition
- 2) Stabilization of insoluble, volatile silicone (cyclomethicone), non-volatile silicone (dimethicone) and other oily materials (sunflower oil, cetearyl octanoate and PPG-2 myristyl ether propionate) in an emulsion

Ingredient	Weight Percent	Function	Trade Name (Supplier)
PART A (heated to 55°C)			
Deionized Water	76.80	Diluent	
Glycerin	2.50	Humectant	
PART B (heated to 55°C)			
PPG-2 Myristyl Ether Propionate	2.00	Emollient	Crodamol PMP (Croda)
Cetearyl Octanoate	3.25	Emollient	Crodamol CAP (Croda)
Sunflower Oil	3.00	Emollient	
Cetyl Alcohol	1.50	Emulsifier	Lanette 16 NF (Henkel)
Cetearyl Alcohol/Ceteareth-20	3.00	Emulsifier	Emulgade 1000 NI (Henkel)
PART C			
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Sodium hydroxide (18%) (to pH 6.5)	0.95	Neutralizer	
PART D (added at 40°C)			
Cyclomethicone (and) Dimethicone	1.00	Lubricant	DC 1401 Fluid (Dow Corning)
PART E			
Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben	1.00	Preservative	Germaben II-E (Sutton)

Properties:

Appearance	White, viscous emulsion
pH	6.0-7.0
Viscosity* (cP)	10,000-20,000
Surfactant Actives (%)	4.5

* Brookfield DV-II + (or RVT) @ 20 rpm, 25°C, #6 spindle

-46-

EXAMPLE 12: Body Lotion

The following formulation is an example of a body lotion. This formulation demonstrates the following:

- 5 1) An aqueous surfactant-based emulsion
- 2) Stabilization of insoluble, volatile silicone (cyclomethicone), non-volatile silicone (dimethicone) and other oily materials (C12-15 alkyl benzoate, octyl stearate, and mineral oil.)

Ingredient	Weight Percent	Function	Trade Name (Supplier)
Part A			
Deionized Water	76.80	Diluent	
Glycerin	2.50	Humectant	
Part B			
Mineral Oil	4.00	Emollient	Drakeol 21 (Penreco)
C12-15 Alkyl Benzoate	2.50	Emollient	Finsolv TN (Finetex)
Octyl Stearate	1.75	Emollient	Cetiol 868 (Henkel)
Cetyl Alcohol	1.50	Emulsifier	Lanette 16 NF (Henkel)
Cetearyl Alcohol/Ceteareth-20	3.00	Emulsifier	Emulgade 1000 NI (Henkel)
Part C			
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Sodium hydroxide (18%)	0.95	Neutralizer	
Part D			
Cyclomethicone (and) Dimethicone	1.00	Lubricant	DC 1401 Fluid (Dow Corning)
Part E			
Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben	1.00	Preservative	Germaben II-E (Sutton)

Properties:

Appearance	White lotion
pH	6.0-7.0
Viscosity* (cP)	15,000-25,000
Surfactant Actives (%)	4.5

* Brookfield DV-II+ (or RVT) @ 20 rpm, 25°C, #6 spindle

-47-

EXAMPLE 13: d-Limonene Cleanser

The following formulation is an example of a d-Limonene cleanser. This formulation demonstrates the following:

- 5 1) An aqueous surfactant-based emulsion composition using the "Back-Acid" formulation technique
- 2) Stabilization and co-emulsification of an insoluble oily material (d-Limonene) in an emulsion with a very low level of surfactant

Ingredient	Weight Percent	Function	Trade Name (Supplier)
Deionized Water	q.s.	Diluent	
Acrylates Crosspolymer (30%)	4.00	Stabilizer	(BFGoodrich)
d-Limonene	25.00	Solvent	Arylessence
Propylene Glycol	1.00	Humectant	
Glycerin	2.00	Humectant	
C ₁₂₋₁₅ Pareth-7	1.00	Surfactant	Neodol 25-7 (Shell)
Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben	1.00	Preservative	Germaben II-E (Sutton Labs)
Sodium hydroxide (18%)	1.20	Neutralizing Agent	
Citric Acid (50%)	0.25	pH adjusted	

Properties:**Appearance**

opaque, white, low viscosity,
sprayable lotion

<u>Addition</u>	<u>Before Citric Acid Addition</u>	<u>After Citric Acid</u>
pH	7.8	6.8
Viscosity* (cP)	6,500	
11,300		
Yield Value** (dynes/cm ²)	520	1,380
Surfactant Actives (%)	1.0	

* Brookfield DV-II+ (or RVT) @ 20 rpm, 25°C, #3 spindle

** Brookfield DV-II+ (or RVT) @ 1 and 0.5 rpm

-48-

EXAMPLE 14: Liquid Detergent

The following formulation is an example of a composition useful for a wide variety of cleansing applications, such as for manual dishwashing. This formulation demonstrates the use of the "Back-Acid" formulation technique to substantially increase the viscosity. Furthermore, the substantial increase in yield value as a result of the "Back-Acid" formulation technique would allow for the suspension of insoluble compounds.

<u>Ingredient</u>	<u>Weight Percent</u>	<u>Function</u>	<u>Trade Name (Supplier)</u>
Deionized Water	Q.S.	Diluent	
Acrylates Crosspolymer (30%)	5.50	Rheology Modifier	(BFGoodrich)
Ammonium lauryl sulfate (28%)	25.00	Surfactant	Standapol A (Henkel)
Sodium Lauryl ether sulfate (2 mole, 25%)	25.00	Surfactant	Standapol ES-2 (Henkel)
Sodium hydroxide (18%)	1.00	pH Adjuster	
Citric acid (50%)	q.s.	pH Adjuster	

Properties:

Appearance

Viscous liquid

<u>Addition</u>	<u>Before Citric Acid Addition</u>	<u>After Citric Acid</u>
pH	7.0	5.0
Viscosity* (cP)	1,825	4,550
Yield Value** (dynes/cm ²)	25	170
Surfactant Actives (%)	13.3	

* Brookfield DV-II + (or RVT) @ 20, # 5 spindle

** Brookfield DV-II + (or RVT) @1 and 0.5 rpm

EXAMPLE 15: Heavy-Duty Liquid Detergent

The following formulation is an example of a composition useful for a wide variety of cleansing applications, such as for manual dishwashing or fabric washing. This formulation demonstrates the use of the "Back-Acid" formulation technique to substantially increase the viscosity. Furthermore, the substantial increase in yield value as a result of the "Back-Acid" formulation technique would allow for the suspension of insoluble compounds.

Ingredient	Weight Percent	Function	Trade Name (Supplier)
Deionized Water	Q.S.	Diluent	
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Sodium lauryl ether sulfate, 3 mole EO (28%)	75.00	Surfactant	Standapol ES-3 (Henkel)
C ₁₂₋₁₃ ethoxylated linear alcohol, 1 mole EO	2.00	Surfactant	Neodol 23-1 (Shell)
Sodium hydroxide (18%)	1.00	pH Adjuster	
Citric acid (50%)	4.00	pH Adjuster	

Properties:

Appearance	viscous liquid
pH	3.0-4.0
Viscosity* (cP)	9,000-10,000
Surfactant Actives (%)	21.0

* Brookfield DV-II + (or RVT) @ 20, # 5 spindle

-50-

EXAMPLE 16: Heavy-Duty Liquid Detergent

The following formulation is an example of a composition useful for a wide variety of cleansing applications, such as for manual dishwashing or fabric washing. This formulation combines the substantially cross-linked alkali-swellable acrylate rheology modifier with a standard cross-linked polyacrylate polymer. This formula further demonstrates the use of the "Back-Acid" formulation technique to substantially increase the viscosity. Furthermore, the substantial increase in yield value as a result of the "Back-Acid" formulation technique would allow for the suspension of insoluble compounds.

Ingredient	Weight Percent	Function	Trade Name (Supplier)
Deionized Water	Q.S.	Diluent	
Acrylates Crosspolymer (30%)	5.00	Rheology Modifier	(BFGoodrich)
Carbomer	0.75	Rheology Modifier	Carbopol EZ-1 (BFGoodrich)
Sodium Lauryl ether sulfate, 2 moles EO (25%)	70.00	Surfactant	Standapol ES-2 (Henkel)
Sodium hydroxide (18%)	1.00	pH Adjuster	
Citric acid (50%)	4.00	pH Adjuster	

Properties:

Appearance viscous liquid
pH 4.0
Viscosity* (cP) 42,000
Surfactant Actives (%) 17.5

* Brookfield DV-II+ (or RVT) @ 20, # 5 spindle

-51-

EXAMPLE 17: Heavy-Duty Liquid Detergent

The following formulation is an example of a composition useful for a wide variety of cleansing applications, such as for fabric washing. This formulation demonstrates the use of the "Back-Acid" formulation technique to substantially increase the viscosity. This example, however, demonstrates the capability to increase the pH of the composition to a very alkaline pH followed by a reduction to a near neutral pH. Furthermore, the substantial increase in yield value as a result of the "Back-Acid" formulation technique would allow for the suspension of insoluble compounds.

Ingredient	Weight Percent	Function	Trade Name (Supplier)
Water	Q.S.	Diluent	
Acrylates Crosspolymer (30%)	7.00	Rheology Modifier	(BFGoodrich)
Alkylbenzene Sulfonic Acid (97%)	13.50	Surfactant	Biosoft S-100 (Stepan)
Sodium lauryl sulfate (29%)	7.50	Surfactant	Standapol WAQ (Henkel)
Sodium lauryl ether sulfate, 2 moles EO (25%)	7.50	Surfactant	Standapol ES-2 (Henkel)
Alkyl polyglucoside (50%)	5.00	Surfactant	Glucopon 600 CS (Henkel)
Coconut fatty acid	3.50	Surfactant	
Triethanolamine (99%)	7.00	pH Adjuster	
Glycerin	2.00	Solvent	
NaOH (50%)	8.60	pH Adjuster	
Citric acid (50%)	8.00	pH Adjuster	

Properties:

Appearance	Viscous gel
pH before citric acid addition	13.0
pH after citric acid addition	8.0
Viscosity* (cP)	15,000
Yield Value** (dynes/cm ²)	180
Surfactant Actives	23.2

* Brookfield DV-II + (or RVT) @ 20, # 5 spindle

** Brookfield DV-II + (or RVT) @ 1 and 0.5 rpm

-52-

Comparative Stability Testing

Select example formulations were formulated with different polymeric rheology modifiers:

Sample	Polymer Code	Description
A	"W"	Acrylates Crosspolymer (present invention)
B		No Polymer
C	"X"	Acrylates/Ceteth-20 Methacrylate Copolymer
D	"Y"	Acrylates/C10-30 Alkyl Acrylate Crosspolymer

The viscosity of experiments made with "No Polymer" were adjusted to the desired viscosity range of each formula using sodium chloride. Equal amounts by weight of "Polymer W" and "Polymer X" were used in each formula. The amount of "Polymer Y" was determined by the desired formulation viscosity.

TABLE 1

Example #	Sample A			Sample B			Sample C			Sample D		
	STAB	SEP	DAY	STAB	SEP	DAY	STAB	SEP	DAY	STAB	SEP	DAY
1	S	0	84	U	10	14	U	2	7	U	10	21
2A	S	0	84	U	6	7	U	2	21	U	6	14
2B	S	0	84	U	10	7	U	2	7	U	2	91
2C	S	0	70	U	10	7	U	4	7	U	4	7
3A	S	0	84	S, LV	0	8	S	0	77	U	2	56
3B	S	0	84	U	10	1	U	10	1	U	10	14
4A	S	0	84	U	10	1	U	10	1	U	10	1
4B	S	0	84	U	10	14	NT			U	10	7
5	S	0	70	U	10	14	NT			U	5	21
6	S	0	84	U	10	1	U	10	7	U	5	7
7	S	0	84	NT			NT			U, PR	--	14

Key:

STAB = Stable/Unstable Rating

S = Stable

U = Unstable

LV = Low Viscosity (initial)

NT = Not Tested

PR = Poor rheology and texture

SEP = Phase Separation Rating Scale

Numerical RatingVisual SeparationStability Interpretation

0

No Separation

Stable

1

Creaming

Borderline Unstable

2

Separation (0.1-0.2cm)

Unstable

5

Separation (0.5cm)

Unstable

10

Separation (4 + cm)

Unstable

DAY = Number of days at 45°C

-53-

As apparent from the data presented in Table 1, the rheology modifying polymer of the present invention (Sample A of each example) yielded improved stability with regard to Examples 1 through 7, whereas the absence of a polymer or the utilization of either polymer X and Y did not yield a stabilized system.

"Back-Acid" Thickening Data

Select example formulations were prepared using the "Back-Acid" formulation technique. The viscosity and yield value measurements were recorded at the initial high pH. Measurements were again recorded after the subsequent addition of the acidic material. Note that the values of viscosity and yield value, as described in Table 2, increase after the acid addition using Polymer W of the present invention. Note that viscosity and yield value do not increase with Polymer X and Polymer Y.

TABLE 2

Example #	Polymer	Reading	pH	Viscosity* (cP)	Yield Value** (dynes/cm ²)
2B	W	Before Citric Acid addition	6.2	1,800	20
		After Citric Acid addition	5.5	7,400	160
3A	W	Before Citric Acid addition	6.5	3,300	22
		After Citric Acid addition	5.0	7,800	180
	X	Before Citric Acid addition	6.5	11,000	28
		After Citric Acid addition	5.2	700	28
9	W	Before Citric Acid addition	6.5	4,600	270
		After Citric Acid addition	4.5	5,500	440
	X	Before Citric Acid addition	6.5	11,000	100
		After Citric Acid addition	4.5	700	25
	Y	Before Citric Acid addition	6.5	6,000	300
		After Citric Acid addition	4.5	2,900	100
13	W	Before Citric Acid addition	7.8	6,500	520
		After Citric Acid addition	6.8	11,300	1,380
14	W	Before Citric Acid addition	7.0	1,825	25
		After Citric Acid addition	5.0	4,550	170

* Brookfield Viscosity @ 20 rpm, Spindle 4

** Brookfield Yield Value @1 and 0.5 rpm

-54-

Improved Pearlescent Appearance

The following formulations were rated according to their pearlescent appearance. The formulas were observed initially (immediately after making), and again after one week of stability testing in 45°C oven. Formulas with the polymer of the present invention (Polymer W) provided an improved pearlescent appearance compared to other polymers (Polymers X and Y) and further maintain this appearance on stability.

TABLE 3
Rating of Pearlescent Appearance of Example Formulations

Example #	Initial Rating				Rating After One Week Aging @ 45°C			
	W	None	X	Y	W	None	X	Y
2A	9	9	9	2	9	1	1	0
2B	8	8	8	1	8	0	0	0
2C	10	10	10	3	10	0	0	0
3B	10	9	9	5	10	0	0	0
4B	10	10	NT	6	10	0	NT	0

Key

NT = Not Tested

Rating Scale for Pearlescent Appearance

Rating	Description
10	Extremely pearlescent appearance. Very intense and vibrant, satiny, elegant, shiny and lustrous.
9	
8	Good pearlescent appearance.
7	
6	
5	Medium pearlescent appearance. Not intense or lustrous.
4	
3	Slightly pearlescent appearance.
2	
1	
0	No pearlescent appearance. Completely opaque and flat

-55-

Photographs of the comparative stability testing of select formulations as shown in data Table I are set forth in the various Figures.

<u>Sample</u>	<u>Polymer Code</u>	<u>Description</u>
A	"W"	Acrylates Crosspolymer (present invention)
B		No Polymer
C	"X"	Acrylates/Ceteth-20 Methacrylate Copolymer
D	"Y"	Acrylates/C10-30 Alkyl Acrylate Crosspolymer

5

FIG. 1 relates to Example 2A (pearlized 2-in-1 conditioning shampoo) stability testing at 45°C for 10 weeks. This photo demonstrates the stability of sample A, and creaming instability of samples B, C, and D. Note that the pearlescent appearance is also diminished in samples B, C, and D.

10

FIG. 2 relates to Example 2C (pearlized 2-in-1 conditioning shampoo with mica) stability testing at 45°C for 8 weeks. This photo demonstrates the enhanced pearlescent appearance and stability of sample A. Creaming instability and a dull appearance are observed in sample C.

15

FIG. 3 relates to Example 2C (pearlized 2-in-1 conditioning shampoo with mica) pearlescent appearance. Note the brilliant appearance of sample A (rating 10), and dull, flat appearance of sample D (rating 0).

20

FIG. 4 relates to Example 2C (pearlized 2-in-1 conditioning shampoo with mica) pearlescent appearance. Top photo is initial appearance, bottom photo is after 12 hours. Note the dull appearance of samples B, C, and D after 12 hours. Sample A maintains brilliant pearlescent appearance.

25

FIG. 5 relates to Example 4A (salicylic acid facial scrub) stability testing at 45°C for 8 weeks. This photo demonstrates

-56-

the stability and suspension of jojoba beads in sample A. Extreme instability and separation of the jojoba beads is observed in samples B, C, and D.

5 FIG. 6 relates to Example 4B (salicylic acid shampoo with mica) stability testing at 45°C for 8 weeks. This photo demonstrates the stability of sample A, as well as an enhanced pearlescent appearance. Extreme instability and sedimentation of mica is observed in samples B and D.

10 FIG. 7 relates to Example 5 (pearlized mild body wash) stability testing at 45°C for 10 weeks. This photo demonstrates the stability of sample A, and vivid phase separation (instability) and sedimentation of samples B and D.

15 FIG. 8 relates to Example 6 (clear bath gel with suspended beads) stability testing at room temperature for 8 weeks. This photo demonstrates the stability and suspension of beads in sample A. Instability and separation of the beads is observed in sample C and D.

20 While in accordance with the Patent Statutes the best mode and preferred embodiment have been set forth, the scope of the invention is not limited thereto but rather by the scope of the claims.

-57-

WHAT IS CLAIMED IS:

1. A stable, aqueous surfactant containing composition, comprising:
 - 5 a. at least one anionic, zwitterionic, amphoteric, nonionic, or cationic surfactant, or combinations thereof;
 - b. at least one substantially crosslinked alkali-swallowable acrylate copolymer rheology modifier;
 - c. water;
 - 10 d. an effective amount of at least one alkaline material to yield a composition having a pH of from about 5 to about 14; and
 - e. an effective amount of a subsequently added acidic material to yield a composition having a reduced pH of
15 from about 1 to about 12.
2. A composition according to Claim 1, wherein the said copolymer is derived from:
 - 20 a. about 20% to about 80% by weight of at least one carboxylic acid monomer comprising acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, aconitic acid, or maleic acid, or combinations thereof;
 - b. about 80% to about 15% by weight of at least one α,β -ethylenically unsaturated monomer, wherein said
25 monomer has the formula:
 - i) $\text{CH}_2=\text{CXY}$,
where X is H and Y is $-\text{COOR}$,
 $-\text{C}_6\text{H}_4\text{R}'$, $-\text{CN}$, $-\text{CONH}_2$, $-\text{Cl}$, $-\text{NC}_4\text{H}_8\text{O}$,

-58-

NH(CH₂)₃COOH, -NHCOCH₃,
 -CONHC(CH₃)₃, -CO-N(CH₃)₂,
 or X is CH₃ and Y is -COOR, -C₆H₄R',
 -CN; or -CH=CH₂;

5 or X is Cl and Y is Cl, and R is C₁-C₁₈
 alkyl, or hydroxy C₂-C₁₈ alkyl,
 R' is H or C₁-C₁₈ alkyl
 or having the formula:

ii) CH₂=CH (OCOR¹);
 10 where R¹ is C₁-C₁₈ alkyl;

or having the formula:

iii) CH₂=CH₂ or CH₂=CHCH₃, and

c. from about 0.01 to about 5% by weight of at least
 one polyunsaturated compound useful in forming a
 15 partially or substantially crosslinked three
 dimensional network.

3. A composition according to Claim 2, wherein the
 amount of the said copolymer is from about 0.1% to about 10%
 20 by weight based upon the total weight of said stable
 composition, and wherein the amount of said surfactant is from
 about 1% to about 80% by weight based upon the total weight
 of said stable composition.

25 4. A composition according to Claim 3, wherein said
 acidic material is citric acid, acetic acid, beta-hydroxy acid,
 salicylic acid, alpha-hydroxy acid, lactic acid, glycolic acid,
 hydrochloric acid, sulfuric acid, nitric acid, sulfamic acid,
 phosphoric acid, or natural fruit acids, or combinations thereof.

-59-

5. A composition according to Claim 4, wherein the said copolymer is derived from:

- a. about 35% to about 65% by weight of acrylic acid or methacrylic acid, or combinations thereof,
- b. about 65% to about 35% by weight of ethylacrylate, or methylacrylate, or combinations thereof, and
- c. about 0.03% to about 3% by weight of polyalkenyl ethers of sucrose or polyalcohols; or trimethylolpropane tri(meth)acrylate, glycidyl methacrylate, N-methylolacrylamide, or combinations thereof.

6. A composition according to Claim 5, including at least one "biologically active" material having pharmaceutical, veterinary, biocidal, herbicidal, pesticidal, or other biological activity.

7. A composition according to Claim 5, including at least one substantially insoluble material requiring suspension or stabilization.

8. A composition according to Claim 7, wherein said substantially insoluble material is a "biologically active" material having pharmaceutical, veterinary, biocidal, herbicidal, pesticidal, or other biological activity.

9. A composition according to Claim 7, wherein said substantially insoluble material is a silicone, or an oily material, or a pearlescent material, or combinations thereof.

-60-

10. A composition according to Claim 9, wherein said insoluble silicone is polydimethylsiloxane, amodimethicone, amodimethicone macroemulsion or microemulsion, dimethicone, 5 dimethiconol (silicone gum), cyclomethicone, phenyltrimethicone, a dimethicone or dimethiconol microemulsion or macroemulsion, an organo polysiloxane, alkoxysilicone, or any combination thereof, wherein the amount of said silicone is from about 0.1 to about 20% by weight based upon the total weight of said stable 10 composition.

11. A composition according to Claim 9, wherein said insoluble pearlescent material is titanium dioxide coated mica, iron oxide coated mica, ethylene glycol monostearate, ethylene 15 glycol distearate, polyethylene glycol distearate, bismuth oxychloride coated mica, myristyl myristate, guanine (fish scales), or glitter (polyester or metallic), or combinations thereof, wherein the amount of said pearlescent material is from about 0.05% to about 10% by weight based upon the total weight of 20 said stable composition.

12. A composition according to Claim 10, wherein said composition is substantially free of a fatty acid, a fatty acid ester, a fatty alcohol, or combinations thereof. 25

13. A stable, aqueous surfactant containing composition, comprising:

a. at least one anionic, zwitterionic, amphoteric, nonionic, or cationic surfactant, or combinations thereof;

-61-

b. at least one substantially crosslinked alkali-swella-
ble acrylate copolymer rheology modifier;

c. water;

5 d. at least one compound which is an insoluble
silicone, or an insoluble oily material, or combinations thereof;
and

e. an effective amount of at least one
neutralizing agent to yield a final pH of from about 5.5 to
about 12.

10

14. A composition according to Claim 13,
wherein the said copolymer is derived from:

15 a. about 20% to about 80% by weight of at
least one carboxylic acid monomer comprising acrylic acid,
methacrylic acid, itaconic acid, fumaric acid, crotonic acid,
aconitic acid, or maleic acid, or combinations thereof;

b. about 80% to about 15% by weight of at
least one α,β -ethylenically unsaturated monomer wherein said
monomer has the formula:

20

i) $\text{CH}_2=\text{CXY}$,

where X is H and Y is $-\text{COOR}$,

$-\text{C}_6\text{H}_4\text{R}'$, $-\text{CN}$, $-\text{CONH}_2$, $-\text{Cl}$, $-\text{NC}_4\text{H}_9\text{O}$,

$-\text{NH}(\text{CH}_2)_3\text{COOH}$, $-\text{NHCOCH}_3$,

$-\text{CONHC}(\text{CH}_3)_3$, $-\text{CO-N}(\text{CH}_3)_2$,

25

or X is CH_3 and Y is $-\text{COOR}$, $-\text{C}_6\text{H}_4\text{R}'$,

$-\text{CN}$; or $-\text{CH}=\text{CH}_2$;

or X is Cl and Y is Cl, and

R is $\text{C}_1\text{-C}_{18}$ alkyl, or hydroxy $\text{C}_2\text{-C}_{18}$

alkyl,

-62-

R' is H or C₁-C₁₈ alkyl

or having the formula:

- ii) CH₂=CH (OCOR¹);
where R¹ is C₁-C₁₈ alkyl;

or having the formula:

- iii) CH₂=CH₂ or CH₂=CHCH₃, and

- c. from about 0.01 to about 5% by weight of at
least one polyunsaturated compound useful
in forming a partially or substantially
crosslinked three dimensional network.

15. A composition according to Claim 14, wherein the
amount of said surfactant is from about 1% to about 80% by
weight based upon the total weight of said stable composition,
and wherein the amount of the said copolymer is from about
0.1% to about 10% by weight based upon the total weight of
said aqueous composition.

16. A stable, aqueous surfactant according to Claim 15,
wherein the said copolymer is derived from

- a. about 35% to about 65% by weight
of acrylic acid or methacrylic acid, or
combinations thereof,
b. about 65% to about 35% by weight
of ethylacrylate, or methylacrylate, or
combinations thereof, and
c. about 0.03% to about 3% by weight
of polyalkenyl ethers of sucrose or
polyalcohols; or trimethylolpropane

-63-

tri(meth)acrylate, glycidyl ethacrylate, N-methylolacrylamide, or combinations thereof.

5 17. A composition according to Claim 14, wherein said
insoluble silicone is polydimethylsiloxane, amodimethicone,
amodimethicone macroemulsion or microemulsion, dimethicone,
dimethiconol (silicone gum), cyclomethicone, phenyltrimethicone,
10 a dimethicone or dimethiconol microemulsion or macroemulsion,
an organo polysiloxane, alkoxysilicone, or any combination
thereof, and wherein the amount of said silicone is from about
0.1 to about 20% by weight based upon the total weight of said
stable composition.

15 18. A composition according to Claim 16, wherein said
insoluble silicone is polydimethylsiloxane, amodimethicone,
amodimethicone macroemulsion or microemulsion, dimethicone,
dimethiconol (silicone gum), cyclomethicone, phenyltrimethicone,
a dimethicone or dimethiconol microemulsion or macroemulsion,
20 an organopolysiloxane, alkoxysilicone, or any combination
thereof, and wherein the amount of said silicone is from about
0.1 to about 20% by weight based upon the total weight of said
stable composition.

25 19. A composition according to Claim 18, wherein said
composition is substantially free of a fatty acid, a fatty alcohol, a
fatty acid ester, or combinations thereof.

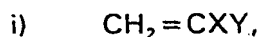
-64-

20. An improved or enhanced pearlescent appearance of a stable, aqueous surfactant containing composition, comprising:

- a. at least one anionic, zwitterionic, amphoteric, nonionic, or cationic surfactant, or combinations thereof;
- b. at least one substantially crosslinked alkali-swellable acrylate copolymer rheology modifier;
- c. water;
- d. at least one pearlescent material; and
- e. an effective amount of at least one neutralizing agent to yield a final pH of from about 5.5 to about 12.

21. A composition according to Claim 20, wherein the said copolymer is derived from:

- a. about 20% to about 80% by weight of at least one carboxylic acid monomer comprising acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, aconitic acid, or maleic acid, or combinations thereof;
- b. about 80% to about 15% by weight of at least one α,β -ethylenically unsaturated monomer wherein said monomer has the formula:



where X is H and Y is $-\text{COOR},$

$-\text{C}_6\text{H}_4\text{R}', -\text{CN}, -\text{CONH}_2, -\text{Cl}, -\text{NC}_4\text{H}_6\text{O},$

-65-

-NH(CH₂)₃COOH, -NHCOCH₃,
-CONHC(CH₃)₃, -CO-N(CH₃)₂,
or X is CH₃ and Y is -COOR, -C₆H₄R',
-CN; or -CH=CH₂;
or X is Cl and Y is Cl, and
R is C₁-C₁₈ alkyl, or hydroxy C₂-C₁₈
alkyl,
R' is H or C₁-C₁₈ alkyl

or having the formula:

ii) CH₂=CH(OCOR¹);
where R¹ is C₁-C₁₈ alkyl;

or having the formula:

iii) CH₂=CH₂ or CH₂=CHCH₃, and

c. from about 0.01 to about 5% by weight of at
least one polyunsaturated compound useful
in forming a partially or substantially
crosslinked three dimensional network.

22. A composition according to Claim 21, wherein the
amount of said surfactant is from about 1% to about 80% by
weight based upon the total weight of said stable composition,
and wherein the amount of the said copolymer is from about
0.1% to about 10% by weight based upon the total weight of
said aqueous composition.

23. A composition according to Claim 22, wherein the
said copolymer is derived from

-66-

- 5 a. about 35% to about 65% by weight of
 acrylic acid or methacrylic acid, or
 combinations thereof,
- b. about 65% to about 35% by weight of
 ethylacrylate, or methylacrylate, or
 combinations thereof, and
- 10 c. about 0.03% to about 3% by weight of
 polyalkenyl ethers of sucrose or polyalcohols;
 or trimethylolpropane tri(meth)acrylate,
 glycidyl methacrylate, N-methylolacrylamide,
 or combinations thereof.

24. A composition according to Claim 21, wherein said
pearlescent material is titanium dioxide coated mica, iron oxide
15 coated mica, ethylene glycol monostearate, ethylene glycol
distearate, polyethylene glycol distearate, bismuth oxychloride
coated mica, myristyl myristate, guanine (fish scales), or glitter
(polyester or metallic), or combinations thereof, wherein the
amount of said pearlescent material is from about 0.05% to
20 about 10% by weight based upon the total weight of said stable
composition.

25. A composition according to Claim 23, wherein said
pearlescent material is titanium dioxide coated mica, iron oxide
25 coated mica, ethylene glycol monostearate, ethylene glycol
distearate, polyethylene glycol distearate, bismuth oxychloride
coated mica, myristyl myristate, guanine (fish scales), or glitter
(polyester or metallic), or combinations thereof, wherein the
amount of said pearlescent material is from about 0.05% to

-67-

about 10% by weight based upon the total weight of said stable composition.

5 26. A composition according to Claim 25, wherein said pearlescent material is titanium dioxide coated mica having an average particle size of from about 2 to about 150 microns in diameter.

10 27. A stable, aqueous temporary hair dye composition comprising:

- 15 a. at least one zwitterionic, amphoteric, nonionic, or cationic surfactant, or combinations thereof;
- b. at least one substantially crosslinked alkali-swella-
 ble acrylate copolymer rheology
 modifier;
- c. water;
- d. at least one cationic hair dye; and
- 20 e. an effective amount of at least one
 neutralizing agent to yield a final pH of from
 about 5 to about 9.

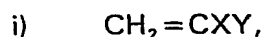
 28. A composition according to Claim 27, wherein the said copolymer is derived from:

- 25 a. about 20% to about 80% by weight of at least one carboxylic acid monomer comprising acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid,

-68-

aconitic acid, or maleic acid, or combinations thereof;

- b. about 80% to about 15% by weight of at least one α,β -ethylenically unsaturated monomer wherein said monomer has the formula:



where X is H and Y is $-\text{COOR}$,

$-\text{C}_6\text{H}_4\text{R}'$, $-\text{CN}$, $-\text{CONH}_2$, $-\text{Cl}$, $-\text{NC}_4\text{H}_6\text{O}$,

$-\text{NH}(\text{CH}_2)_3\text{COOH}$, $-\text{NHCOCH}_3$,

$-\text{CONHC}(\text{CH}_3)_3$, $-\text{CO-N}(\text{CH}_3)_2$,

or X is CH_3 and Y is $-\text{COOR}$, $-\text{C}_6\text{H}_4\text{R}'$,

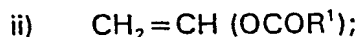
$-\text{CN}$; or $-\text{CH}=\text{CH}_2$;

or X is Cl and Y is Cl, and

R is C_1 - C_{18} alkyl, or hydroxy C_2 - C_{18} alkyl,

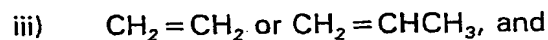
R' is H or C_1 - C_{18} alkyl

or having the formula:



where R^1 is C_1 - C_{18} alkyl;

or having the formula:



- c. from about 0.01 to about 5% by weight of at least one polyunsaturated compound useful in forming a partially or substantially crosslinked three dimensional network.

29. A composition according to Claim 28, wherein the amount of said surfactant is from about 1% to about 80% by

-69-

weight based upon the total weight of said stable composition, and wherein the amount of the said copolymer is from about 0.1% to about 10% by weight based upon the total weight of said aqueous composition.

5

30. A composition according to Claim 29, wherein the said copolymer is derived from

- 10 a. about 35% to about 65% by weight of acrylic acid or methacrylic acid, or combinations thereof,
- b. about 65% to about 35% by weight of ethylacrylate, or methylacrylate, or combinations thereof, and
- 15 c. about 0.03% to about 3% by weight of polyalkenyl ethers of sucrose or polyalcohols; or trimethylolpropane tri(meth)acrylate, glycidyl methacrylate, N-methylolacrylamide, or combinations thereof.

20

31. A composition according to Claim 28, wherein said cationic hair dye is an azo dye, or an anthraquinone dye, or combinations thereof, and wherein the amount of said hair dye is from about 0.1% to about 5% by weight based upon the total weight of the stabilized composition.

25

32. A composition according to Claim 31, wherein said azo dye is Basic Brown 16 (CI 12250), Basic Brown 17 (CI 12251), Basic Red 76 (12245), Basic Yellow 57 (CI 12719), and wherein said anthraquinone dye is Basic Blue 99 (CI 56059).

-70-

33. A composition according to Claim 30, wherein said cationic hair dye is an azo dye, or an anthraquinone dye, or combinations thereof, and wherein the amount of said hair dye is
5 from about 0.1% to about 5% by weight based upon the total weight of the stabilized composition.

34. A composition according to Claim 33, wherein said azo dye is Basic Brown 16 (CI 12250), Basic Brown 17 (CI
10 12251), Basic Red 76 (12245), Basic Yellow 57 (CI 12719), and wherein said anthraquinone dye is Basic Blue 99 (CI 56059).

35. A composition according to Claim 13, whereby said composition includes at least one pearlescent material, or at least
15 one cationic hair dye, or combinations thereof, and said composition is stable.

36. A composition according to Claim 18, whereby said composition includes at least one pearlescent material, or at least
20 one cationic hair dye, or combinations thereof, and said composition is stable.

37. A composition according to Claim 36, wherein said pearlescent material is titanium dioxide coated mica, iron oxide
25 coated mica, ethylene glycol monostearate, ethylene glycol distearate, polyethylene glycol distearate, bismuth oxychloride coated mica, myristyl myristate, guanine (fish scales), or glitter (polyester or metallic), or combinations thereof, and wherein the amount of said pearlescent material is from about 0.05% to

-71-

about 10% by weight based upon the total weight of said composition.

5 38. A composition according to Claim 24, whereby said composition additionally contains at least one insoluble silicone, or at least one soluble silicone, or at least one soluble cationic hair dye, or combinations thereof, and said composition is stable.

10 39. A composition according to Claim 31, whereby said composition additionally contains at least one insoluble silicone, or at least one soluble silicone, or at least one pearlescent material, or combinations thereof, and wherein said composition is stable.

15 40. A composition according to Claim 5, wherein said composition is a personal care cleansing composition, wherein said acid is salicylic acid or alpha-hydroxy acid, and wherein the amount of said acid is from about 0.2 to about 6 % by weight.

20 41. A composition according to Claim 5, wherein said composition is a personal care emulsion composition, wherein said acid is an alpha-hydroxy acid or beta-hydroxy acid, and wherein the amount of said acid is from about 0.2% to about 15 % by weight.

25 42. A composition according to claim 37, wherein said composition is a personal care cleansing composition, and wherein the amount of said insoluble silicone is from about 0.1 % to about 5% by weight, and wherein the amount of said

-72-

pearlescent material is from about 0.05% to about 3% by weight.

5 43. A composition according to claim 17, including at least one cationic conditioning polymer, and wherein the amount of said cationic polymer is from about 0.01 to 5 % by weight.

10 44. A composition according to claim 43, wherein said cationic conditioning polymer is cationic guar gum, polyquaternium-4, polyquaternium-6, polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-16, polyquaternium-24, polyquaternium-39, or combinations thereof.

15 45. A composition according to Claim 43, including at least one pearlescent material.

20 46. A composition according to Claim 45, wherein said pearlescent material is titanium dioxide coated mica having an average particle size of from about 2 to about 150 microns in diameter.

25 47. A composition according to Claim 7, wherein said composition is an anti-dandruff shampoo, wherein said substantially insoluble material requiring suspension or stabilization is zinc pyrithione, and wherein the amount of said zinc pyrithione is from about 0.1% to 5% by weight.

-73-

48. A composition according to Claim 2, including at least one substantially insoluble material requiring suspension or stabilization.

5 49. A composition according to Claim 48, wherein said substantially insoluble material is a silicone, or an oily material, or a pearlescent material, or combinations thereof.

10 50. A composition according to Claim 49, wherein said insoluble silicone is polydimethylsiloxane, amodimethicone, amodimethicone macroemulsion or microemulsion, dimethicone, dimethiconol (silicone gum), cyclomethicone, phenyltrimethicone, a dimethicone or dimethiconol microemulsion or macroemulsion, an organosiloxane, alkoxysilicone, or any combination thereof, 15 wherein the amount of said silicone is from about 0.1 to about 20% by weight based upon the total weight of said stable composition.

20 51. A composition according to Claim 49, wherein said insoluble pearlescent material is titanium dioxide coated mica, iron oxide coated mica, ethylene glycol monostearate, ethylene glycol distearate, polyethylene glycol distearate, bismuth oxychloride coated mica, myristyl myristate, guanine (fish scales), or glitter (polyester or metallic), or combinations thereof, 25 wherein the amount of said pearlescent material is from about 0.05% to about 10% by weight based upon the total weight of said stable composition.

-74-

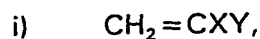
52. A process for preparing a stable, aqueous surfactant containing composition, comprising the steps of:

- 5
- a. forming a mixture comprising at least one anionic, zwitterionic, amphoteric, nonionic, or cationic surfactant, or combinations thereof; at least one substantially crosslinked alkali-swellable acrylate copolymer rheology modifier; and water;
- 10
- b. neutralizing said mixture with an effective amount of an alkaline material to increase the pH of said mixture to at least about 5; and
- c. adding an effective amount of an acidic material to reduce the pH of said mixture from about 0.5 to about 5 pH units.

15

53. A process according to Claim 52, wherein the said copolymer is derived from:

- 20
- a. about 20% to about 80% by weight of at least one carboxylic acid monomer comprising acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, aconitic acid, or maleic acid, or combinations thereof;
- 25
- b. about 80% to about 15% by weight of at least one α,β -ethylenically unsaturated monomer wherein said monomer has the formula:



-75-

where X is H and Y is $-\text{COOR}$,

$-\text{C}_6\text{H}_4\text{R}'$, $-\text{CN}$, $-\text{CONH}_2$, $-\text{Cl}$, $-\text{NC}_4\text{H}_9\text{O}$,

$-\text{NH}(\text{CH}_2)_3\text{COOH}$, $-\text{NHCOCH}_3$,

$-\text{CONHC}(\text{CH}_3)_3$, $-\text{CO-N}(\text{CH}_3)_2$,

or X is CH_3 and Y is $-\text{COOR}$, $-\text{C}_6\text{H}_4\text{R}'$,

$-\text{CN}$; or $-\text{CH}=\text{CH}_2$;

or X is Cl and Y is Cl, and

R is C_1 - C_{18} alkyl, or hydroxy C_2 - C_{18}

alkyl,

R' is H or C_1 - C_{18} alkyl

or having the formula:

ii) $\text{CH}_2=\text{CH}(\text{OCOR}^1)$;

where R^1 is C_1 - C_{18} alkyl;

or having the formula:

iii) $\text{CH}_2=\text{CH}_2$ or $\text{CH}_2=\text{CHCH}_3$, and

- c. from about 0.01 to about 5% by weight of at least one polyunsaturated compound useful in forming a partially or substantially crosslinked three dimensional network.

54. A process according to Claim 53, wherein the amount of said substantially alkali-swelling crosslinked polymer is from about 0.1% to about 10% by weight based upon the total weight of said stable composition, and wherein the amount of said surfactant is from about 1% to about 80% by weight based upon the total weight of said stable composition.

55. A process according to Claim 54, wherein the said copolymer is derived from:

-76-

- 5 a. about 35% to about 65% by weight of
 acrylic acid or methacrylic acid, or
 combinations thereof,
- b. about 65% to about 35% by weight of
 ethylacrylate, or methylacrylate, or
 combinations thereof, and
- 10 c. about 0.03% to about 3% by weight of
 polyalkenyl ethers of sucrose or polyalcohols;
 or trimethylolpropane tri(meth)acrylate,
 glycidyl methacrylate, N-methylolacrylamide,
 or combinations thereof.

56. A process according to Claim 54, wherein said
acidic material is citric acid, acetic acid, beta-hydroxy acid,
15 salicylic acid, alpha-hydroxy acid, lactic acid, glycolic acid,
hydrochloric acid, sulfuric acid, nitric acid, sulfamic acid, or
phosphoric acid, or natural fruit acids, or combinations thereof.

57. A process according to Claim 56, including forming
20 a stable composition of a substantially insoluble material requiring
suspension or stabilization.

58. A composition according to Claim 57, wherein said
substantially insoluble material is a silicone, or an oily material, or
25 a pearlescent material, or combinations thereof.

59. A composition according to Claim 58, wherein said
insoluble silicone is polydimethylsiloxane, amodimethicone,
amodimethicone macroemulsion or microemulsion, dimethicone,

-77-

dimethiconol (silicone gum), cyclomethicone, phenyltrimethicone, a dimethicone or dimethiconol microemulsion or macroemulsion, an organopolysiloxane, alkoxysilicone, or any combination thereof, wherein the amount of said silicone is from about 0.1 to
5 about 20% by weight based upon the total weight of said stable composition.

60. A composition according to Claim 58, wherein said insoluble pearlescent material is titanium dioxide coated mica,
10 iron oxide coated mica, ethylene glycol monostearate, ethylene glycol distearate, polyethylene glycol distearate, bismuth oxychloride coated mica, myristyl myristate, guanine (fish scales), or glitter (polyester or metallic), or combinations thereof, wherein the amount of said pearlescent material is from about
15 0.05% to about 10% by weight based upon the total weight of said stable composition.

1/8

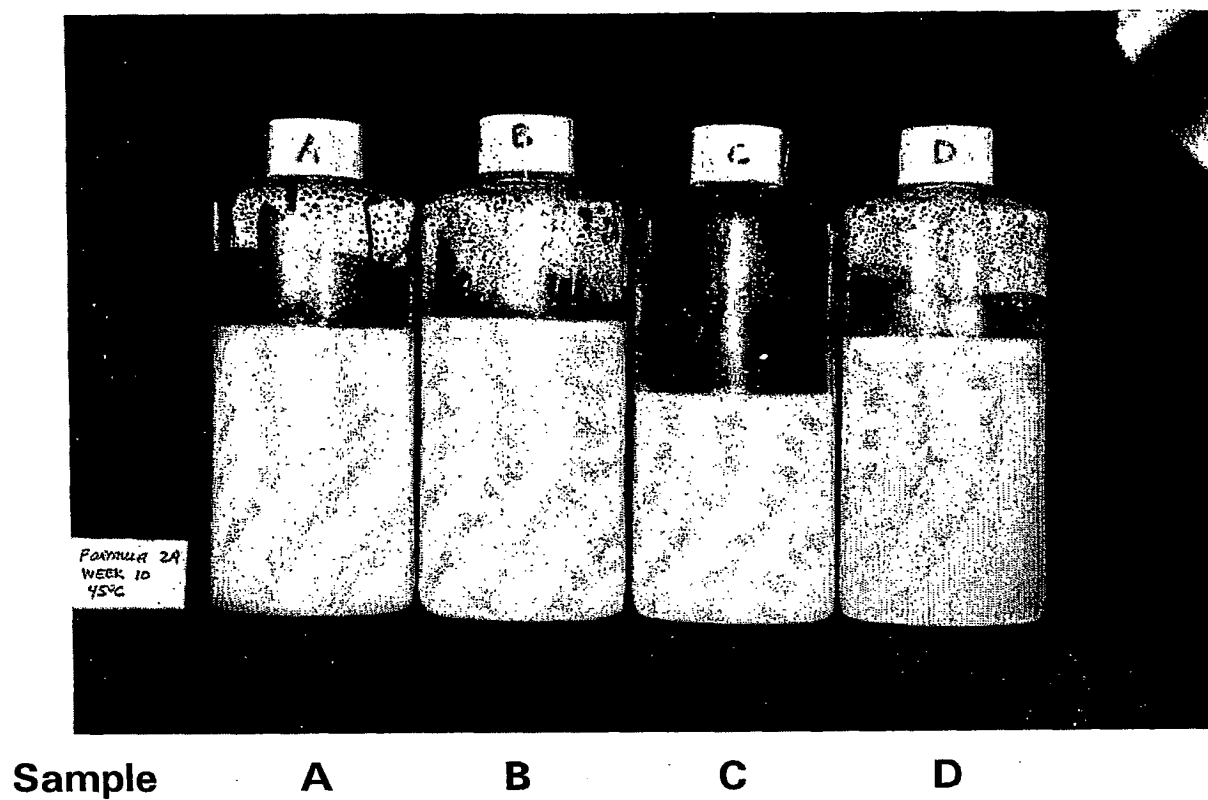
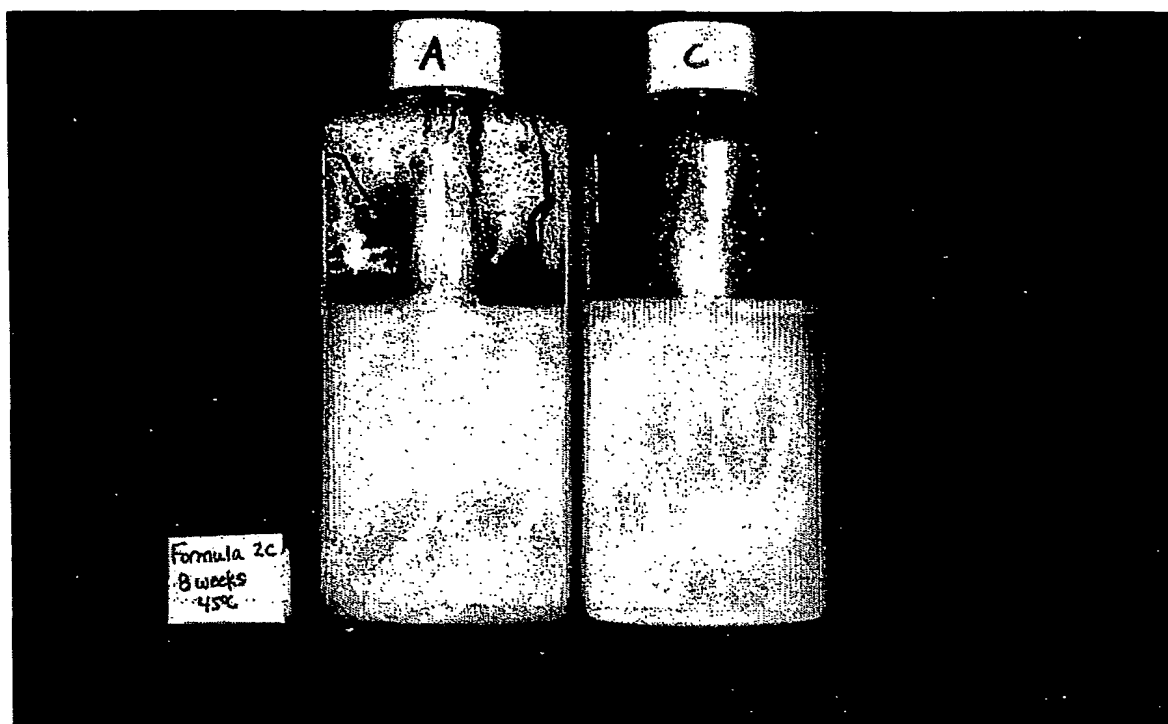


FIG. 1

2/8



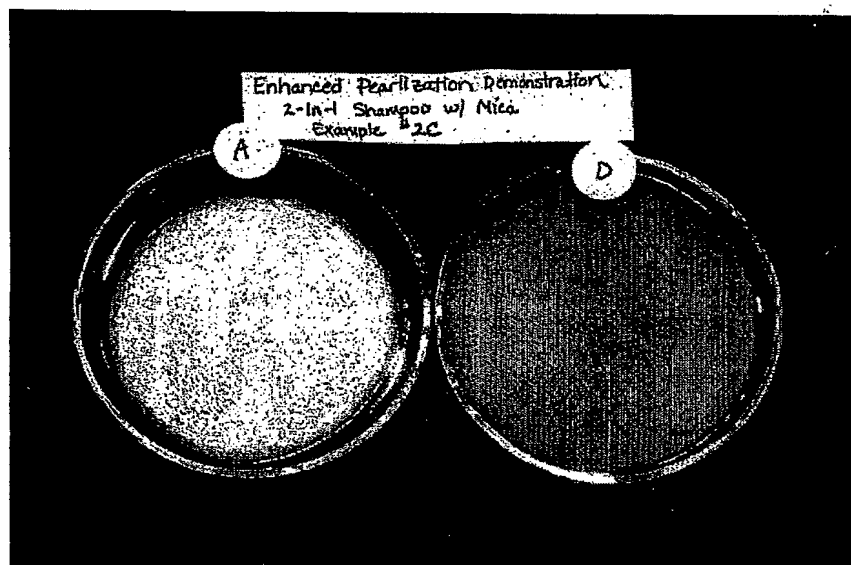
Sample

A

C

FIG. 2

Sample A
Polymer
"W"



Sample D
Polymer
"Y"

FIG. 3

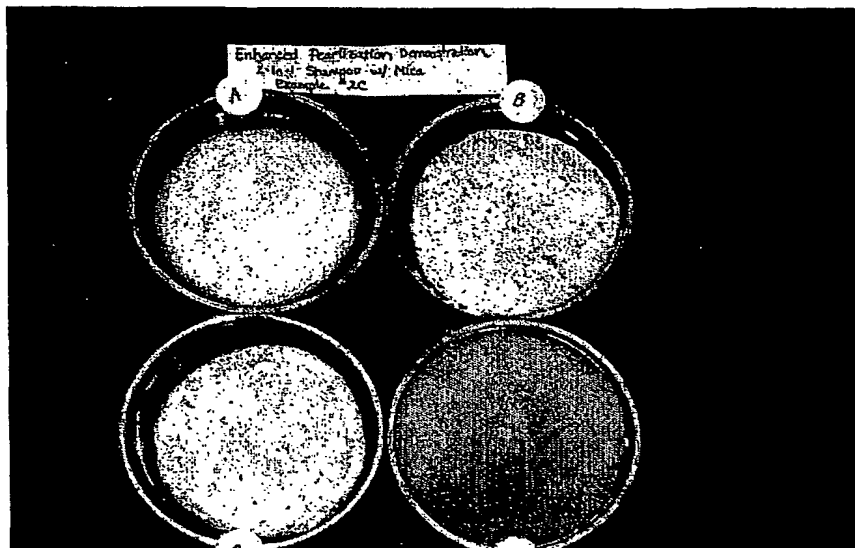
4/8

Sample A:
Polymer
"W"

Sample C:
Polymer
"X"

Sample B:
No
Polymer

Sample D:
Polymer
"Y"



Sample A:
Polymer
"W"

Sample C:
Polymer
"X"

Sample B:
No
Polymer

Sample D:
Polymer
"Y"

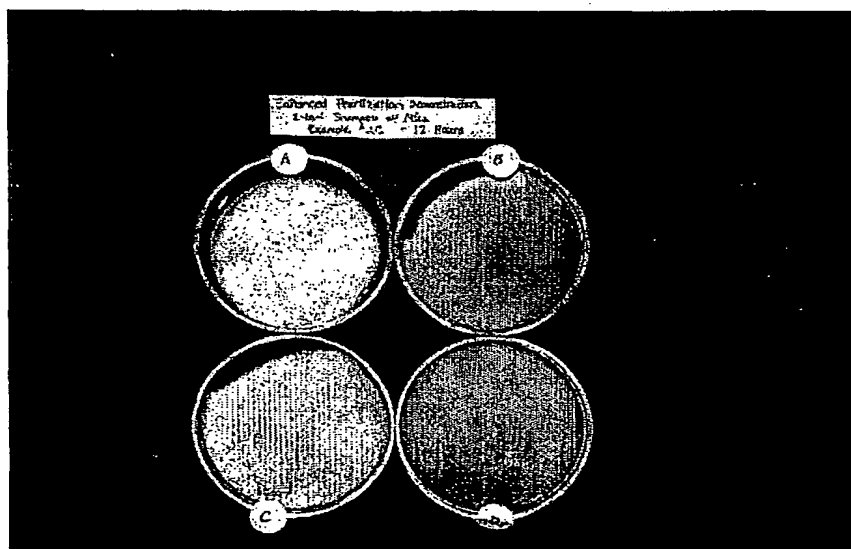
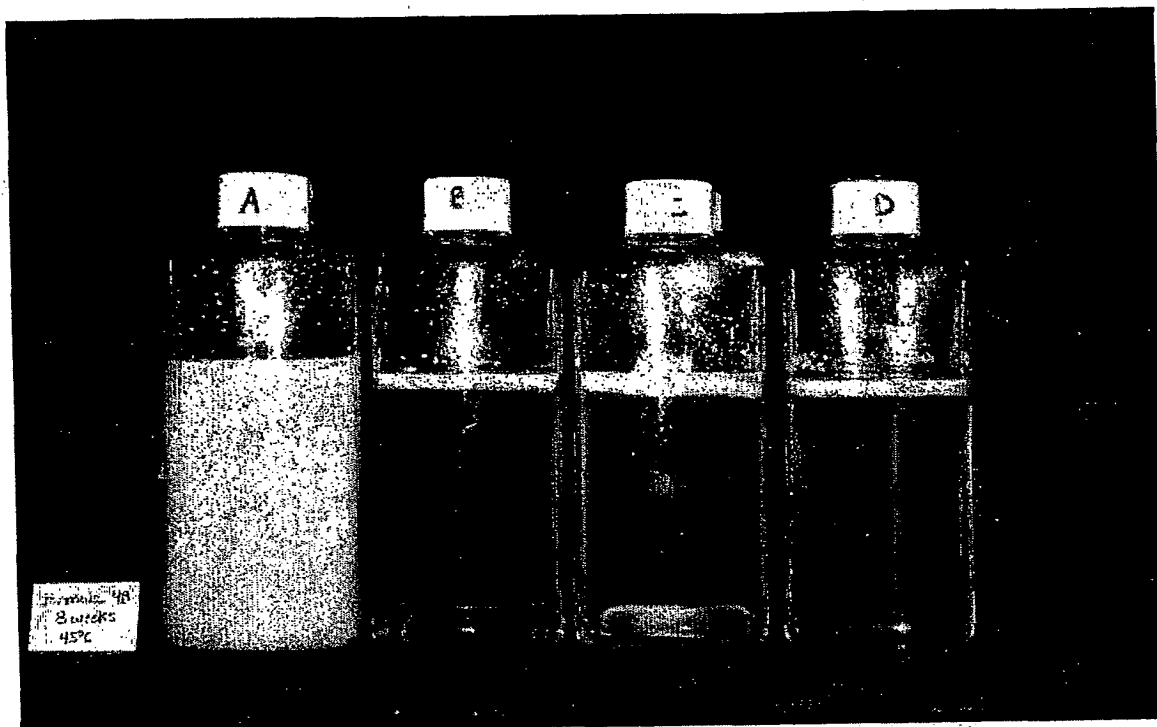


FIG. 4

5/8



Note correction: formula

Sample

A

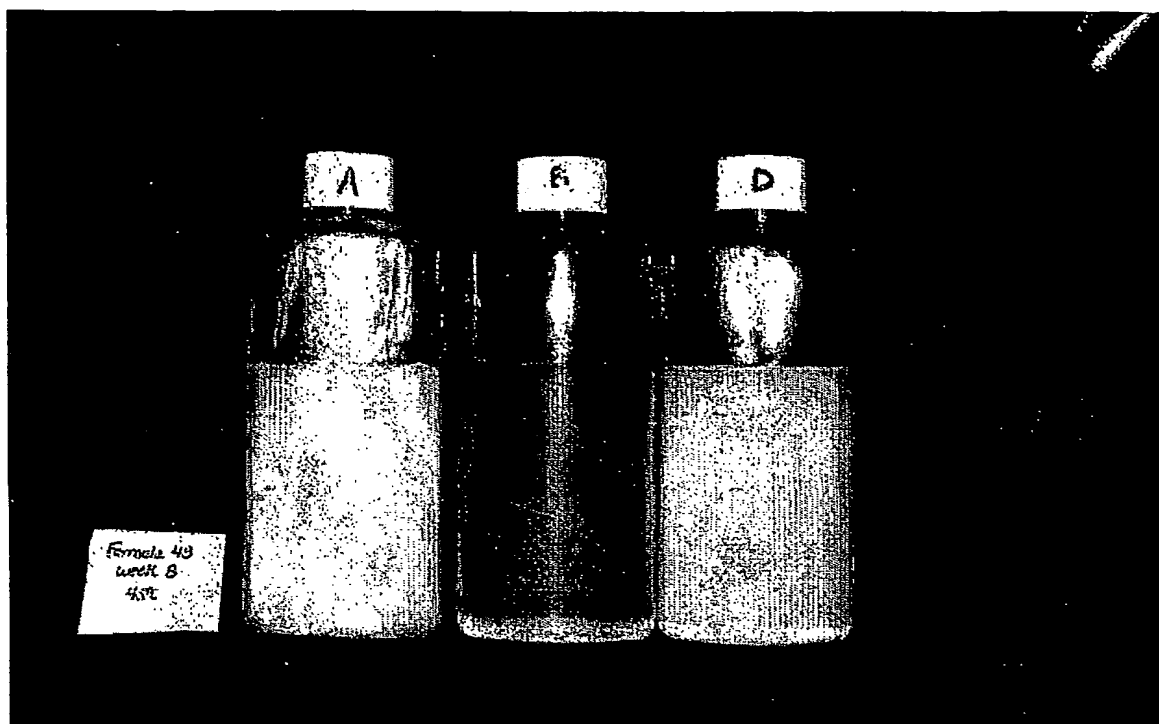
B

C

D

FIG. 5

6/8



Sample

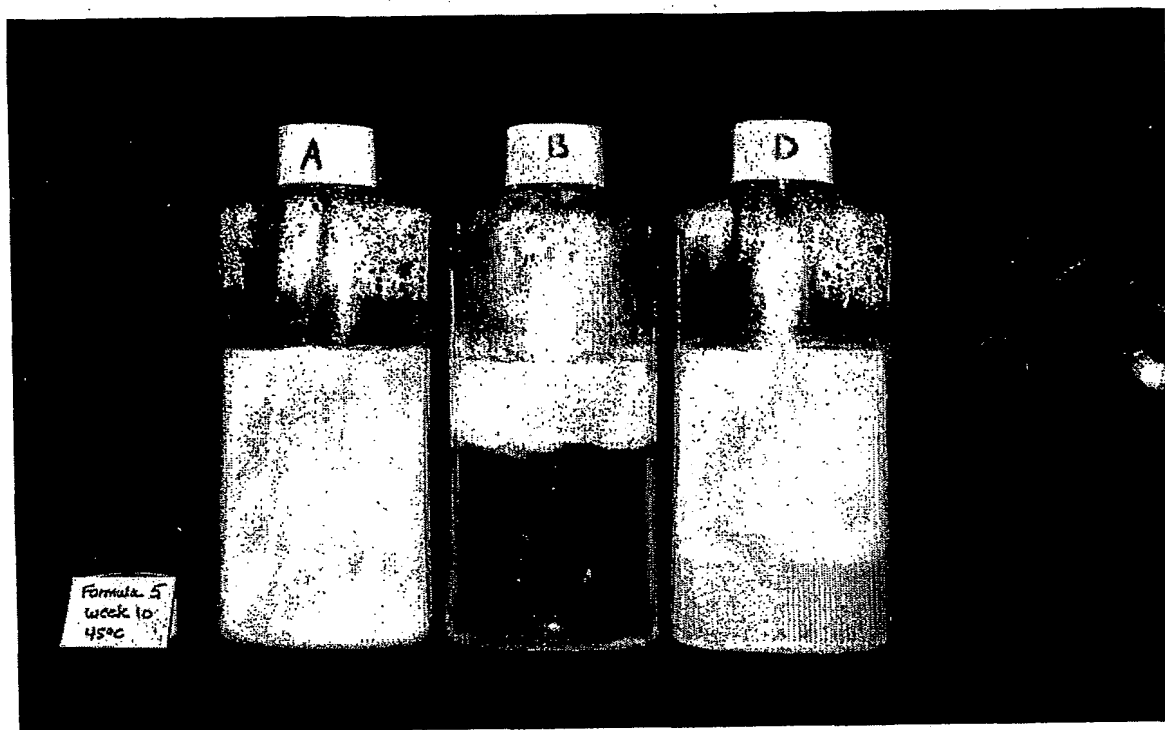
A

B

D

FIG. 6

7/8



Sample

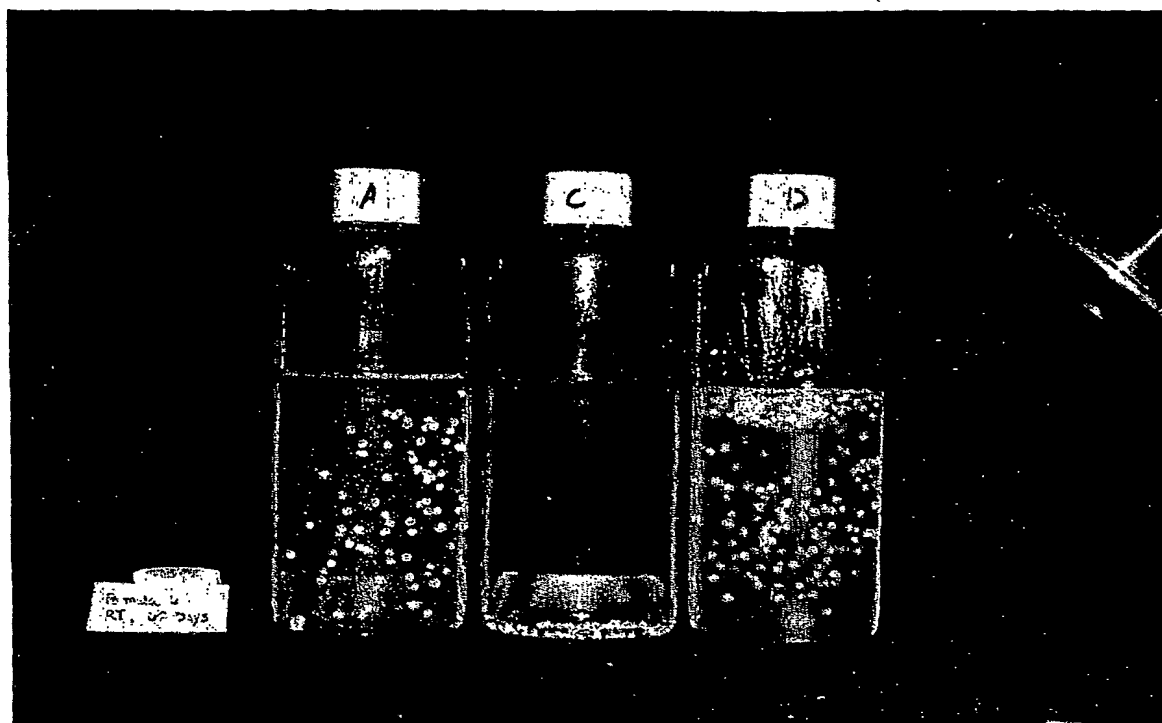
A

B

D

FIG. 7

8/8



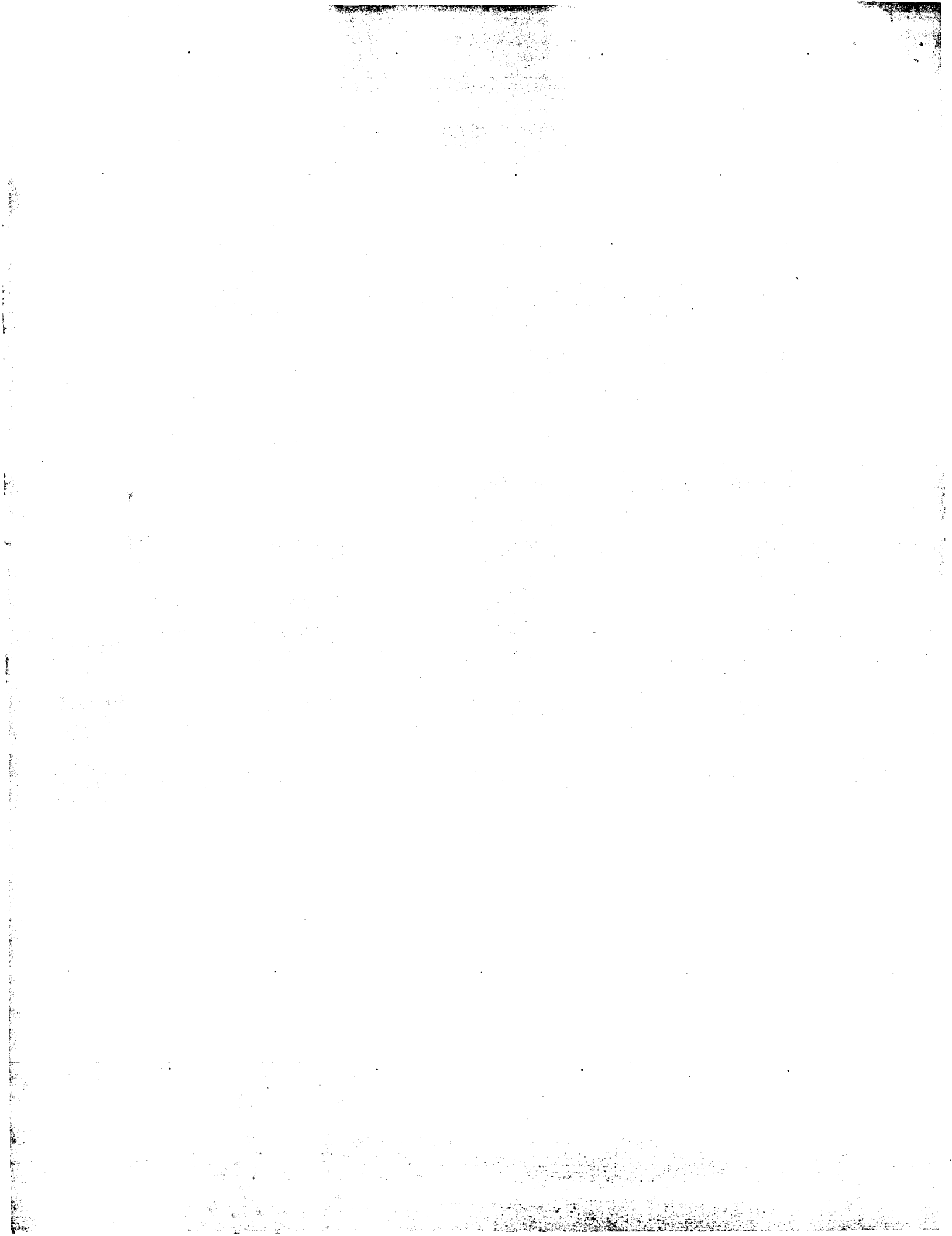
Sample

A

C

D

FIG. 8



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 October 2001 (18.10.2001)

PCT

(10) International Publication Number
WO 01/076552 A3

(51) International Patent Classification⁷: **A61K 7/50**,
7/48, 7/06

(21) International Application Number: PCT/US01/40480

(22) International Filing Date: 11 April 2001 (11.04.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/547,595 11 April 2000 (11.04.2000) US

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant: NOVEON IP HOLDINGS CORP. [US/US];
9911 Brecksville Road, Cleveland OH 44141-3247 (US).

Published:
— with international search report

(72) Inventors: SCHMUCKER-CASTNER, Julie, F.; 15207 Parkwood Lane, Strongsville, OH 44136 (US). AM-BUTER, Hal; 3887 Ridge Road, Medina, OH 44256 (US). SNYDER, Marcia; 4580 Greenlawn, Stow, OH 44224 (US). WEAVER, Ashley, A.; 1301 S. Scott Street #329, Arlington, VA 22204 (US). KOTIAN, Sahira, V.; 40249 Dow Estates, Gonzales, LA 70737 (US).

(88) Date of publication of the international search report:
19 September 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(74) Agent: DUNLAP, Thoburn, T.; Noveon, Inc., Law Department, 9911 Brecksville Road, Cleveland, OH 44141-3247 (US).

(54) Title: STABLE AQUEOUS SURFACTANT COMPOSITIONS

(57) Abstract: A stable, aqueous composition containing a substantially crosslinked alkali-swellable acrylate copolymer rheology modifier, a surfactant, an alkaline material, and various compounds therein, as for example substantially insoluble materials requiring suspension or stabilization, such as a silicone, an oily material, or a pearlescent material. Additionally, this invention also relates to the formation of a rheologically and phase stable cationic hair dye composition. The invention further relates to the incorporation of an acidic material after the addition of an alkaline material to reduce the pH of the composition without negatively impacting the viscosity of the composition.

WO 01/076552 A3

THIS PAGE BLANK (USPTO)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/40480

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/50 A61K7/48 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 024 946 A (DUBIEF CLAUDE ET AL) 15 February 2000 (2000-02-15) column 7, line 37 - line 56; claims 1,2,9,10,15,17; examples ---	1-3, 6-10, 13-15, 17,48-50
A	EP 0 463 780 A (UNILEVER PLC ;UNILEVER NV (NL)) 2 January 1992 (1992-01-02) cited in the application page 4, line 37 -page 5, line 31; claims 1,5-8,13 --- -/--	1-3,5,7, 9-26, 35-38, 42-51



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

20 November 2001

Date of mailing of the international search report

28/11/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Angiolini, D

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/40480

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 658 577 A (FOWLER TIMOTHY JOHN ET AL) 19 August 1997 (1997-08-19) column 18, line 18 -column 19, line 46; claims 1,7,10; example 5 -----	1-5,7,9, 10, 13-18, 40-44, 48-50
A	US 4 529 773 A (DUPRE JEAN ET AL) 16 July 1985 (1985-07-16) cited in the application claims 1,6; table II -----	1-5, 52-56

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 01/40480

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6024946	A	15-02-2000	FR 2676923 A1	04-12-1992
			AT 126429 T	15-09-1995
			AU 669330 B2	06-06-1996
			AU 1883592 A	08-01-1993
			CA 2110571 A1	10-12-1992
			DE 69204162 D1	21-09-1995
			DE 69204162 T2	18-01-1996
			EP 0587637 A1	23-03-1994
			ES 2075701 T3	01-10-1995
			WO 9221316 A1	10-12-1992
			JP 6510273 T	17-11-1994
EP 0463780	A	02-01-1992	GB 2245279 A	02-01-1992
			AT 133064 T	15-02-1996
			AU 636231 B2	22-04-1993
			AU 7846091 A	02-01-1992
			BR 9102568 A	21-01-1992
			CA 2022901 A1	21-12-1991
			DE 69116448 D1	29-02-1996
			DE 69116448 T2	20-06-1996
			EP 0463780 A2	02-01-1992
			ES 2082139 T3	16-03-1996
			GR 3019253 T3	30-06-1996
			IN 171889 A1	30-01-1993
			JP 1900717 C	27-01-1995
			JP 4243812 A	31-08-1992
			JP 6021051 B	23-03-1994
			KR 9614778 B1	19-10-1996
			US 6106816 A	22-08-2000
			ZA 9104743 A	24-02-1993
US 5658577	A	19-08-1997	US 5534265 A	09-07-1996
			AT 186208 T	15-11-1999
			AU 705770 B2	03-06-1999
			AU 3330195 A	22-03-1996
			CA 2198476 A1	07-03-1996
			CN 1159160 A	10-09-1997
			CZ 9700601 A3	13-08-1997
			DE 69513183 D1	09-12-1999
			EP 0777465 A1	11-06-1997
			JP 10505062 T	19-05-1998
			WO 9606596 A1	07-03-1996
US 4529773	A	16-07-1985	AT 18251 T	15-03-1986
			AU 552193 B2	22-05-1986
			AU 1254083 A	22-09-1983
			CA 1203140 A1	15-04-1986
			DE 3362231 D1	03-04-1986
			EP 0089213 A2	21-09-1983
			JP 1783394 C	31-08-1993
			JP 4075278 B	30-11-1992
			JP 58189299 A	04-11-1983

THIS PAGE BLANK (USPTO)